Table I

hkl, Relative Intensities (I/I_0), and Interplanar Spacings of Tl_2TiCl_6

hkl	I/I_0	*d*, Å.	*hkl*	I/I_0	*d*, Å.
111	3	5.64	642	5	1.314
200	8	4.90	800	1	1.225
220	10	3.48	733	1	1.186
311	<1	2.95	822	2	1.157
222	10	2.84	662	3	1.126
400	9	2.45	840	3	1.097
420	6	2.194	911	<1	1.072
422	7	2.004	664	1	1.047
440	7	1.738	844	2	1.003
531	<1	1.660	933	<1	0.9890
600	4	1.638	10 2 0	2	0.9638
620	5	1.554	951	1	0.9455
622	6	1.480	953	<1	0.9083
444	4	1.418	10 4 2	<1	0.8958
711	2	1.363	880	<1	0.8688

62.7. Calcd. for Tl_2TiCl_6: Tl, 61.08; Ti, 7.16; Cl, 31.76. Found: Tl, 61.2; Ti, 7.2; Cl, 31.6.

The properties of the potassium salt agreed with the findings of Schossberger[6] and Flengas.[7]

Engel[2] reported that the thallium salt could not be obtained from aqueous solutions. Morozov and Toptygin[9] prepared the thallium salt from aqueous solutions without giving details about the preparation.

We found that the thallium salt is stable in dry air and decomposes slowly in moist air (relative humidity ≈60%) at room temperature. The thallium(I) hexachlorotitanate is not soluble in water; after a few minutes it is hydrolyzed as indicated by the color change from yellow to white. The X-ray diffraction pattern of Tl_2TiCl_6 showed that the compound is isomorphous with Tl_2PtCl_6. The interplanar spacings, estimated relative intensities, and *hkl* values of the X-ray diffraction pattern of Tl_2TiCl_6 are listed in Table I. Its crystal structure is face-centered cubic with a space group O^5_H-Fm3m. There was some difficulty in accurately measuring the back reflection lines of the X-ray diagram because of their relatively low intensity and broadening. This was probably caused by the small crystallite size or crystal defects of the prepared compounds. The lattice constant, a_0, was calculated as the average from all *d* values neglecting the lines with $2\theta < 45°$. The lattice constant was found to be $a_0 = 9.804 \pm 0.008$ Å. This value is slightly higher than Engel predicted ($a_0 = 9.793$ Å.).[2]

The formation of K_2TiCl_6 and Tl_2TiCl_6 in fused $SbCl_3$ can be considered an acid–base reaction between the "base" KCl or TlCl and the "acid" $TlCl_4$ in the solvent $SbCl_3$. $TiCl_4$ behaves probably as a "Lewis acid" in fused $SbCl_3$. Another type of acid–base reaction in fused $SbCl_3$ was described by Jander and Swart.[11]

Preliminary experiments showed that by choice of suitable compounds and "semisalt" solvent systems, it was possible to prepare other hexahalotitanates which are either not or difficultly accessible by the methods mentioned above. The results of these investigations will be published later.

Acknowledgment.—Miss Irene Corvin performed the X-ray analysis.

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Studies on the Synthesis and Crystal Structure of 1,4-Selenothiane

By J. D. McCullough and Phillip Radlick

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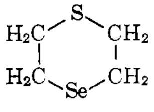
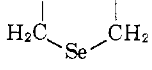
The synthesis of 1,4-selenothiane (I) was first reported by Gibson and Johnson.[1] These authors obtained I in "small yield" from the reaction of β,β′-dichlorodiethyl sulfide (mustard gas) on aqueous sodium selenide after unsuccessful attempts to obtain the desired product from the reaction of β,β′-dichlorodiethyl selenide (selenium mustard) with aqueous sodium sulfide. The poor yield in the one case and the failures in the other probably were due to the inability of Se^{-2} and S^{-2} to compete favorably with water in reacting with the cyclic sulfonium and selenonium ions, respectively.[2,3] In contrast, Johnson and Gibson obtained good yields of 1,4-selenoxane (II)[4] from the reaction of β,β′-dichlorodiethyl ether with aqueous sodium selenide. In this case the reaction path does not appear to involve a cyclic oxonium ion and Se^{-2} is able to compete favorably with water in replacing chlorine. It occurred to the present authors that the yield of 1,4-selenothiane might be greatly improved if β,β′-dichlorodiethyl sulfide and sodium selenide were brought together in a nonaqueous medium. The present note describes an improved synthesis of I based on this hypothesis and presents the results of a preliminary X-ray diffraction study of single crystals of the solid.


I


II

Experimental

Synthesis of 1,4-Selenothiane.—Sodium (4.6 g., 0.20 g.-atom) was dissolved in absolute ethanol (450 ml.) in a 1-l. flask equipped with a mercury-sealed stirrer, reflux condenser, gas dispersion tube, and dropping funnel. By means of a stream of nitrogen, the hydrogen selenide prepared by the action of water on aluminum selenide[5] (18 g., 0.062 mole) was passed into the alcoholic solution while the latter was being stirred. To the resulting brown solution, still under nitrogen gas, β,β′-dichlorodiethyl sulfide (15 g., 0.094 mole) in absolute ethanol (200 ml.) was added dropwise, with stirring, over a period of 10 min. The mixture was refluxed 2 hr., yielding a white precipitate. The mixture was then cooled, the solid was filtered off and washed with ether, and the washings were added to the filtrate. The

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[1] C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 1529 (1933).

[2] P. D. Bartlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).

[3] E. S. Gould and J. D. McCullough, *ibid.*, **73**, 1105 (1951).

[4] J. D. A. Johnson and C. S. Gibson, *J. Chem. Soc.*, 266 (1931).

[5] J. D. McCullough and N. W. Tideswell, *J. Am. Chem. Soc.*, **76**, 3091 (1954).

filtrate was concentrated under reduced pressure to yield a crop of light yellow crystals. The yield of dried product was 6.8 g. or about 44% based on mustard gas. Sublimation of the product yielded a white solid, m.p. 107.0–107.5°.

Anal. Calcd. for C_4H_8SSe: C, 28.74; H, 4.82; S, 19.18. Found: C, 28.56; H, 4.96; S, 19.35.

The sublimation left a yellow residue (10–15% of total yield) which is presumably a polymeric material and/or polyselenide which would account for the yellow color of the crude product.

X-Ray Diffraction.—Small, single crystals of I suitable for X-ray diffraction studies were obtained by slow evaporation of solutions in methanol. Selected crystals were sealed in thin-walled capillaries to prevent vaporization. Zero and upper level Weissenberg photographs about the *b* or prism axis were prepared by use of copper radiation. Precession photographs of the *hk*0 and 0*kl* nets were also prepared. These photographs strongly suggested isomorphism of I with 1,4-diselenane[6] and with 1,4-dithiane.[7] Measurement of the films gave the unit cell dimensions shown in Table I.

TABLE I

CRYSTALLOGRAPHIC AND PHYSICAL DATA ON THE ISOMORPHOUS SERIES: 1,4-DITHIANE, 1,4-SELENOTHIANE, AND 1,4-DISELENANE

	$C_4H_8S_2$	C_4H_8SSe	$C_4H_8Se_2$
a, Å.	6.763 ± 0.002	6.867 ± 0.006	6.97 ± 0.02
b, Å.	5.464 ± 0.005	5.552 ± 0.010	5.62 ± 0.02
c, Å.	7.844 ± 0.003	7.956 ± 0.006	8.01 ± 0.02
β, deg.	92.67 ± 0.04	93.13 ± 0.10	93.6 ± 0.1
Vol. of unit cell, $Å.^3$	289.7	302.9	313
d, g. $cm.^{-3}$	1.377	1.832	2.27
M.p., °C.	112	107.0–107.5	113.0–113.5

Discussion

Crystallographic and physical data on the isomorphous series 1,4-dithiane, 1,4-selenothiane, and 1,4-diselenane are listed for ready comparison in Table I. Gibson and Johnson[1] noted that the melting point of I is not depressed by addition of 1,4-dithiane and concluded that solid solutions are formed. This conclusion is in keeping with the results of the X-ray studies.

The presence of two molecules of I per unit cell in the space group $P2_1/n$ requires that the molecules be centrosymmetric. This requirement can be satisfied only by a random disorder in which the crystallization process fails to differentiate between the S and Se ends of the molecules. This disorder would not only obscure the true positions of sulfur and selenium, but also those of the carbon atoms, since the C–S and C–Se distances are different. For this reason a detailed structural study of I by X-ray diffraction appears to have little merit.

Acknowledgments.—The authors wish to thank the National Science Foundation for financial assistance (Grant No. NSF-G 12884), Heather King for the chemical analysis, and Hanelore Maddox for preparing and measuring one of the Weissenberg photographs.

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

[7] R. E. Marsh, *Acta Cryst.*, **8**, 91 (1955).

Correspondence

Partial Charge and Bonding Energy

Sir:

Bond energy (*H*) may reasonably be expected to be greater the more polar the bond, the higher its order (*n*), and the shorter the bond length (*R*). This expectation is realized in many binary halides and calcides. When the partial charge on halogen, δ_X, is plotted graphically *vs.* RH/n, a straight line connecting the free halogen X_2 with the salt NaX is found to include most of the binary halides. This is true of chlorides, bromides, and iodides. A linear relationship holds also for fluorides but F_2 with its unusually low bond energy understandably lies off the line. Results for chlorides are shown in Fig. 1; those for the other halides are closely similar. The equations for these relationships are of the form

$$\delta_X = A\frac{RH}{n} + B \qquad (1)$$

When δ_X is expressed as fraction of electronic charge *e*, *H* as kcal., and *R* in a.u., then *A*, of dimension $1/e$, and *B*, of dimension *e*, are constants having the following values: fluorides −0.00130, 0.066; chlorides −0.00114, 0.065; bromides −0.00111, 0.068; and iodides −0.00105, 0.071.

The partial charge is calculated[1] from the principle of electronegativity equalization[2] supplemented by two assumptions. The principle of electronegativity equalization may be stated: *When two or more atoms initially different in electronegativity form a compound, their electronegativities change to the same intermediate value in the compound.* This intermediate value is taken to be the geometric mean of the electronegativities of all the component atoms before compound formation. The reduction in electronegativity of the initially more electronegative element, in a binary compound, results from its acquisition of a partial negative charge through uneven sharing of the valence electrons. Similarly, the initially less electronegative element becomes more electronegative through its retention of less than a half share of the valence electrons and thus in effect by its acquisition of a partial positive charge. To estimate these partial charges quantitatively it is necessary to assume (1) that electronegativity varies linearly with partial charge, and (2) that a particular bond has a fixed and known ionicity. The first assumption is reasonable in view of what is known of the relationship between ionization energies and electronegativities of cations.[3] The second assumption must, in

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[1] R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960, p. 42.

[2] R. T. Sanderson, *Science*, **114**, 670 (1951).

[3] Reference 1, p. 40.