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An X-Ray Study of Triphenylselenonium Chloride[1]

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The study described in the present communication was undertaken as a part of a program involving crystal structure studies on organoselenium compounds. The structures of four compounds of the type R_2SeX_2, where R is phenyl or *p*-tolyl and X is chlorine or bromine, have already been reported from this Laboratory.[2,3,4] Since no structures of the type R_3SeX had been reported in the literature, it was considered of interest to undertake the present investigation.

Preparation of the Crystals.—The triphenylselenonium chloride used in this study was prepared by the method of Leicester and Bergstrom.[5] The product was recrystallized twice from methyl ethyl ketone, dried at 100° and identified as anhydrous triphenylselenonium chloride through volumetric determination of the chloride present. Crystals suitable for the preparation of X-ray diffraction photographs were obtained by the slow evaporation of a solution of the substance in a mixture of equal parts of absolute alcohol and benzene. The crystals were needle-like, elongated in the *c* direction with principal faces of the form (110).

The X-Ray Study.—Sets of rotation and Weissenberg photographs were prepared about all three orthorhombic axes by use of filtered copper radiation. For photographs about the *a* and *b* axes, it was necessary to cleave the crystals perpendicular to the *c* axis. The dimensions of the unit-cell (based on $CuK_\alpha = 1.5418$ Å.) were found to be $a = 10.93$ Å., $b = 10.38$ Å., $c = 14.51$ Å. all ± 0.03 Å. The approximate density of the crystals was found to be 1.4 g./cc. by flotation in mixtures of benzene and carbon tetrachloride. The density computed from the X-ray data on the assumption of $4(C_6H_5)_3SeCl$ per unit-cell is 1.395 g./cc. The only systematic absences were found to be h0l with *h* odd and 0*kl* with $(k + l)$ odd, indicating the space-group to be either Pna-C_{2v}^9 or Pnam-D_{2h}^{16}.

While the space-group Pna places no symmetry restrictions on the structure of the $(C_6H_5)_3SeCl$ molecule (or of the $(C_6H_5)_3Se^+$ ion), the space-group Pnam requires either a center of symmetry or a mirror when only four structural units are placed in the unit-cell. The selenium and chlorine atoms, each in fourfold positions, would thus be restricted to *z* parameters of 0, $^1/_4$, $^1/_2$ and $^3/_4$. Although there were no grounds for eliminating Pnam in the earlier considerations, it was definitely ruled out later by the Patterson projections on (100) and (010). These projections indicated differences of 0.140 and 0.360 in the *z* parameters of Se and Cl rather than the values $^1/_4$ or $^1/_2$ required by the space-group Pnam. The space-groups is accordingly Pna.

Since the projection on (001) is the only centrosymmetric projection of the space-group Pna, it was decided to prepare a Fourier summation on this face. The selenium atoms are by far the heaviest atoms in the substance and will accordingly determine the signs of the majority of the structure factors. From an inspection of the intensities of reflections of the type *h*00 and 0*k*0, it was possible to assign approximate values of the *x* and *y* parameters of the selenium atom. By use of these values, the signs of all structure factors of the type *hk*0 were tentatively fixed and these were then used to prepare the Fourier summation on (001). This summation showed, in addition to a large peak due to the selenium atom, a smaller peak doubtless due to chlorine. Using the resulting chlorine parameters, the signs of five structure factors were changed, and a second and final Fourier summation was prepared. This projection is shown in Fig. 1. It should be pointed out that the constant term $F(000)$ was not included in the summation, with the result that the size of the selenium peak is disproportionately large.

Since Fourier projections on the other two faces of the unit cell are not centrosymmetric, these summations may be obtained only with considerable difficulty and were not attempted. However, Patterson projections on (100) and (010) are readily carried out and these were accordingly prepared. As is typical of a compound containing one atom considerably heavier than any other, little detail was obtained from the Patterson projections. In addition to the Se–Se peaks which occurred at positions consistent with the *x* and *y* parameters of the selenium atom, the only other peaks were of appropriate height and position to represent Se–Cl interactions. From these peaks, it was possible to obtain the difference in the *z* parameters of the selenium and chlorine atoms. Due to the polar character of the *c* axis, it is necessary to fix arbitrarily the *z* parameter for one atom and to base all other *z* parameters on this value. On this basis, the *z* parameter for selenium was taken as zero. Values for the other parameters of the selenium and chlorine atoms are given in Table I. These values account satisfactorily for all of the peaks appearing on the Patterson projections. Due to the poorer resolution of

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[1] Based in work performed under Contract N6onr-275 between the Office of Naval Research and the University of California, Los Angeles.

[2] J. D. McCullough and G. Hamburger, THIS JOURNAL, **63**, 803 (1941).

[3] J. D. McCullough and G. Hamburger, *ibid.*, **74**, 508 (1942).

[4] J. D. McCullough and R. E. Marsh, *Acta Crystallographica*, **3**, 42 (1950).

[5] H. M. Leicester and F. W. Bergstrom, THIS JOURNAL, **51**, 3587 (1929).

the Patterson projections, a larger uncertainty is given to the z parameter of the chlorine atom than to the other parameters.

Since there are 72 carbon atoms at unknown locations in the unit cell, no attempt was made to calculate structure factors. If these were calculated on the basis of the selenium and chlorine atoms alone, only crude qualitative agreement with observed intensities could be expected.

TABLE I

PARAMETERS FOR HEAVY ATOMS IN TRIPHENYLSELENONIUM CHLORIDE

	Se	Cl
x	0.166 ± 0.002	0.359 ± 0.003
y	.002 ± .002	.201 ± .003
z	(0)	.150 ± .005

Discussion

The projections give no more than vague indications of the positions of the phenyl groups. This is unfortunate since it prevents a determination of the configuration about the selenium atom. The closest observed approach of chlorine to selenium, 3.60 ± 0.05 Å., does, however, give definite indication that the structure is built up of $(C_6H_5)_3Se^+$ and Cl^- ions rather than of molecules containing covalent Se–Cl bonds. This conclusion is drawn from the fact that the sum of the normal single-bond covalent radii for Se and Cl is only 2.16 Å.[6] and from the observed Se–Cl bonded separation of 2.38 Å. in $(NH_4)_2SeCl_6$[7] and in $(p\text{-}CH_3\text{-}C_6H_4)_2SeCl_2$.[4] The discrepancy between the observed covalently-bonded distances and the radius sum has been discussed by Pauling[8] and by the present authors.[4]

In order to determine the configuration of the bonds about the selenium atom in the selenonium ion, it is planned to make more complete structural studies of other selenonium salts. It is hoped that it will be possible to find a salt possessing crystal symmetry more suitable for a complete structural investigation. Further work on the present compound would be extremely lengthy, since it is evident that three-dimensional work on the polar crystal would be necessary in order to locate the carbon atoms accurately.

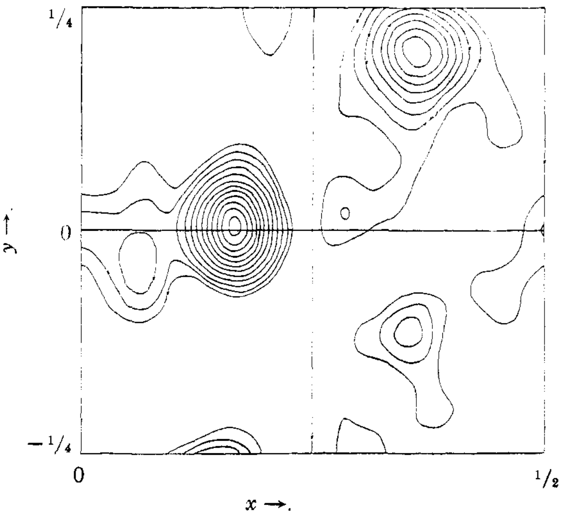

Fig. 1.—Fourier projection on (001): the contour interval on selenium is twice that used on remainder of plot.

The conclusion regarding the ionic character of triphenylselenonium chloride is in keeping with its high solubilities in water and in other polar solvents and its relatively low solubilities in carbon tetrachloride and in carbon bisulfide. The reverse solubility behavior is observed for the covalently-bonded diphenylselenium dihalides which dissolve only slowly in water and then apparently with complete hydrolysis as indicated by the low pH values of the resulting solutions. The pH values of aqueous triphenylselenonium chloride solutions are, by contrast, only slightly below 7.

Summary

Orthorhombic crystals of anhydrous triphenylselenonium chloride have been studied by means of Weissenberg photographs prepared about all three crystallographic axes. The space-group was found to be Pna-C_{2v}^9 with $4(C_6H_5)_3SeCl$ in the unit-cell. The minimum observed Se–Cl separation of 3.60 Å. is conclusive evidence that the substance is ionic and that it probably contains $(C_6H_5)_3Se^+$ and Cl^- ions. It has not been possible to locate the carbon atoms and hence the present study does not permit conclusions to be drawn regarding the structure of the triphenylselenonium ion.

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(6) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940. p. 164.

(7) G. Engel, *Z. Krist.*, **90**, 341 (1935).

(8) Ref. 6, p. 184.