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The Crystal Structure of *p*-Chlorobenzeneseleninic Acid

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Crystals of *p*-chlorobenzeneseleninic acid are monoclinic holohedral with $a = 12{\cdot}14$, $b = 5{\cdot}14$, $c = 12{\cdot}55$ Å, and $\beta = 111° 5'$. The space group is $P2_1/c$ and there are four molecules in the unit cell. The structure was determined by means of projections along [010] and [001] which were refined by least-squares routines carried out on SWAC. The molecular structure and the hydrogen-bonded columns or chains along the screw axes are identical to those found in the unsubstituted acid. The two crystals are related by a type of pseudo isomorphism which is discussed in some detail.

Introduction

During the recent determination of the structure of benzeneseleninic acid (Bryden & McCullough, 1954), X-ray diffraction photographs of crystals of several *para*-substituted benzeneseleninic acids were also prepared with the thought that these substances might be isomorphous with the unsubstituted acid, and in this way be of aid in arriving at a satisfactory trial structure. In particular, it was hoped that the *p*-chloro acid might give helpful information regarding the tilt of the axis of the benzene ring with respect to (010). It is an interesting fact that this latter goal was actually realized in spite of the fact that crystals of the *p*-chloro acid are not isomorphous with those of the unsubstituted acid.

The present study of the structure of *p*-chlorobenzeneseleninic acid was carried out mainly as an aid in the precise determination of the structure of benzeneseleninic acid, but it was of interest also to investigate the similarities of, and the differences between, the two structures. Since quite accurate values for the bond distances and bond angles in this type of molecule were found in the three-dimensional study of benzeneseleninic acid reported earlier, the present study was carried only through the refinement of projections along [010] and [001].

Crystallography of the acids

Rotation and Weissenberg photographs of crystals of *p*-chlorobenzeneseleninic acid, *p*-nitrobenzeneseleninic acid, and *p*-tolueneseleninic acid showed that these are isomorphous with each other in the monoclinic space group $P2_1/c$. The cell dimensions of these acids, together with those of the unsubstituted acid, are shown in Table 1. These constants are based on Cu $K\alpha = 1{\cdot}542$ Å.

Table 1. *Cell dimensions of benzeneseleninic acids*

Acid	a (±0·03 Å)	b (±0·02 Å)	c (±0·03 Å)	β (±15′)
Benzeneseleninic	10·29 Å	5·14 Å	12·63 Å	99° 15′
p-Toluene-seleninic	12·32	5·14	12·52	111 40
p-Chlorobenzene-seleninic	12·14	5·14	12·55	111 05
p-Nitrobenzene-seleninic	12·34	5·14	12·66	113 50

Since the unsubstituted acid also crystallizes in $P2_1/c$, it was at first thought that the acids were all isomorphous. However, the large discrepancy in the angle β (approximately 12°) and the differences in structure which soon became apparent definitely ruled out this possibility. By setting the *p*-chloro acid up as $P2_1/n$, the cell constants are quite similar to those of benzeneseleninic acid (see Table 4), but the arrangement of symmetry elements is then different. This interesting relationship between the two structures is discussed later.

The density of the *p*-chloro acid was found by flotation in mixtures of ethylene bromide and carbon tetrachloride to be 2·03 g.cm.$^{-3}$. The density calculated from the X-ray data and the assumption of four molecules in the unit cell is 2·044 g.cm.$^{-3}$.

Determination of the approximate structure

From zero-level Weissenberg photographs about the b axis, values for $F^2(h0l)$ on a relative scale were obtained. These values were used to prepare a Patterson projection on (010). By making the reasonable assumption that the molecules form chains about the twofold screw axes as in benzeneseleninic acid, the Patterson projection indicated the following parameters for the heavier atoms:

	x	z
Se	0·089	0·379
Cl	0·450	0·650

By use of these parameters, phases for the 160 $F(h0l)$ values were computed and a Fourier projection on (010) was prepared. This projection showed all atoms except hydrogen clearly resolved. One refinement involving changes of sign of a few F values gave the projection shown in Fig. 1. The x and z parameters given in Set A, Table 2, were derived from this projection. At this stage, the value of R in the expression

$$R = \Sigma|(|F_o|-|F_c|)|\div\Sigma|F_o|$$

was 0·20 when an isotropic temperature factor, $B = 2{\cdot}32\times10^{-16}$ cm.², was used.

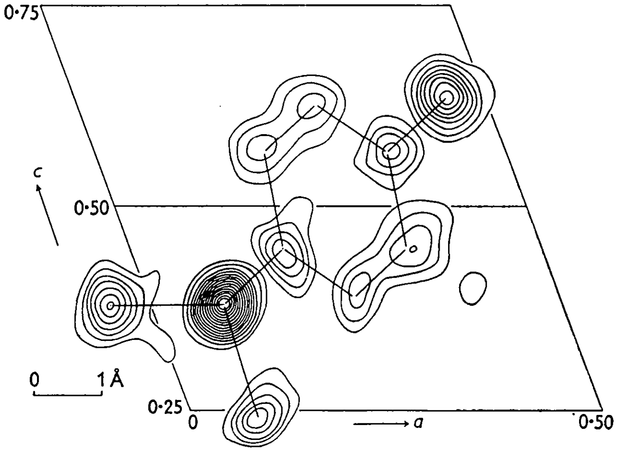

Fig. 1. Fourier projection on (010). Contour intervals: 1·5 e.Å^{-2} for carbon and oxygen, 3·0 e.Å^{-2} for chlorine, 5 e.Å^{-2} for selenium. The zero contour is not shown.

An examination of the upper-level Weissenberg photographs about the b axis showed that reflections of the type $k+l = 2n+1$ were weak and did not extend to high values of sin θ. This same feature was noted in benzeneseleninic acid and was due to the fact that the y parameter of selenium was nearly zero (−0·0021). The y parameter for selenium in the p-chloro acid was therefore taken tentatively as zero, a circumstance which prevents the use of selenium alone to determine the phases of the $F(hk0)$ values for which k is odd. However, a Fourier projection along [001] was prepared, using only those $F(hk0)$ values for which k is even. This projection has additional symmetry that would not be found on a complete Fourier projection, but it did give a good indication of the location of the chlorine atom. The possible y parameters for chlorine were 0·097, 0·403, 0·597, and 0·903, of which only the last value gives a reasonable Se–Cl distance across the ring, namely, 6·4 Å.

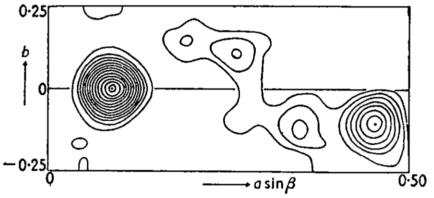

Fig. 2. Fourier projection along [001]. Contour intervals as in Fig. 1

Table 2. *Atomic parameters and their standard deviations for p-chlorobenzeneseleninic acid*

Atom	Set	x	y	z
Se	A	0·0890	0·9979	0·3810
	B	0·0886	0·9977	0·3804
	C	0·0889	0·9969	0·3803
	σ (c)	0·0004	0·0029	0·0004
Cl	A	0·4500	0·8970	0·6340
	B	0·4510	0·9011	0·6370
	C	0·4520	0·9014	0·6375
	σ (c)	0·0012	0·0065	0·0011
O_1	A	0·0790	0·0410	0·2390
	B	0·0836	0·0018	0·2480
	C	0·0826	0·0410	0·2449
	σ (c)	0·0022	(0·02–)	0·0022
O_2	A	0·9520	0·1440	0·3820
	B	0·9547	0·1543	0·3814
	C	0·9552	0·1440	0·3799
	σ (c)	0·0022	(0·02–)	0·0023
C_1	A	0·1870	0·2700	0·4480
	B	0·1882	0·2001	0·4481
	C	0·1886	0·2700	0·4470
	σ (c)	0·0026	(0·03–)	0·0031
C_2	A	0·2480	0·4060	0·3900
	B	0·2607	0·4095	0·4015
	C	0·2622	0·4060	0·4050
	σ (c)	0·0035	(0·03–)	0·0037
C_3	A	0·3350	0·5970	0·4480
	B	0·3479	0·5881	0·4521
	C	0·3445	0·5970	0·4554
	σ (c)	0·0042	(0·03–)	0·0037
C_4	A	0·3530	0·6730	0·5670
	B	0·3566	0·6844	0·5604
	C	0·3523	0·6730	0·5643
	σ (c)	0·0041	(0·03–)	0·0042
C_5	A	0·2900	0·5480	0·6250
	B	0·2854	0·5745	0·6205
	C	0·2920	0·5480	0·6194
	σ (c)	0·0051	(0·03–)	0·0030
C_6	A	0·2050	0·3450	0·5670
	B	0·2091	0·3169	0·5684
	C	0·2144	0·3450	0·5706
	σ (c)	0·0045	(0·03–)	0·0032

This chlorine parameter made it possible to calculate signs with considerable certainty for all $F(hk0)$ values. The resulting complete Fourier projection along [001], Fig. 2, shows the selenium and chlorine atoms well resolved, but gives little information regarding the y parameters of the carbon and oxygen atoms.

Refinement of the structure

The structure was refined by application of the method of least squares to the $h0l$ and $hk0$ data (Sparks, Prosen, Kruse & Trueblood, 1956). The parameters listed as Set A in Table 2 served as the starting values, the y parameters for oxygen and carbon being the ones found for these atoms in benzeneseleninic acid.

Justification for this is given later. Five least-squares cycles were carried out on each projection, using the isotropic temperature factor given above. During this process, the value of R dropped to 0·169 for the (010) projection and 0·126 for the [001] projection. The parameters at this stage of refinement are those listed under Set B in Table 2. The x parameters, determined independently in the refinement of each projection, agreed within their standard deviations at this stage. These standard deviations were only slightly greater than those given for Set C in Table 2.

Four more least-squares cycles were then performed on the $h0l$ data, making use of individual anisotropic temperature factors on each atom. These factors were of the type

$$\exp\,[-(B_{11}h^2+B_{13}hl+B_{33}l^2)]\;.$$

The starting values were derived from the isotropic value given earlier. The x and z parameters resulting from this further refinement are listed in Set C of Table 2 together with their standard deviations derived from the determinant coefficients (Shoemaker, Donohue, Schomaker & Corey, 1950). The value of R for the (010) projection was reduced to 0·125 by the final refinement.

The anisotropic temperature factors and their standard deviations resulting from the final least-squares refinement of the projection on (010) are given in Table 3. The factors for selenium and chlorine are of possible significance, also perhaps those for oxygen. However, the factors for carbon probably should not be taken too seriously. The B_{13} factor for C_2 is unexpectedly large and no structurally significant explanation is proposed. Probably the erratic temperature factors for the lighter atoms represent an attempt on the part of the least-squares refinement to cover up errors in the intensity data. Also, the hydrogen atoms were not included and there were undoutedly errors caused by absorption. Most significant is the fact that the least-squares refinement with anisotropic temperature factors changed the x and z positional parameters by less than the standard deviations in these quantities in all but four cases, and in these the shift was but little more than the standard deviation.

Table 3. *Anisotropic temperature factors and their standard deviations, from least-squares refinement of projection on* (010)

(Values in Å²)

Atom	B_{11}	σ_{11}	B_{13}	σ_{13}	B_{33}	σ_{33}
Se	2·8	0·2	4·4	0·3	2·5	0·2
Cl	3·3	0·4	1·2	0·7	4·5	0·5
O_1	2·5	0·8	5·1	1·2	3·3	0·8
O_2	0·9	0·8	−2·6	1·4	2·6	0·9
C_1	0·6	0·8	1·0	1·5	2·3	1·1
C_2	3·3	1·2	19·0	1·5	6·9	1·0
C_3	2·7	1·5	2·9	2·1	3·3	1·3
C_4	2·9	1·5	3·4	2·2	4·1	1·4
C_5	4·8	2·3	0·5	2·4	0·8	0·9
C_6	5·8	1·8	6·1	2·0	2·1	1·0

It is evident that the y parameters of the lighter atoms from the least-squares refinements of the $hk0$ data (Set B) are not very reliable. This is not surprising in view of the fact that these atoms are not resolved on the Fourier projection along [001]. Furthermore, it should be noted that there were only 54 observed $F(hk0)$ values. In the least-squares refinement with an isotropic temperature factor there are 20 variables, but this number increases to 50 when anisotropic temperature factors are included. Clearly the results of such a treatment of the $hk0$ data would not be very significant. However, in the case of the $h0l$ data, there are 160 observed reflections so that the further refinement is justified.

Considering all factors, it was decided that the best y parameters for carbon and oxygen atoms in the *p*-chloro acid are those from the three-dimensional study of the unsubstituted acid. This decision was based on the following facts:

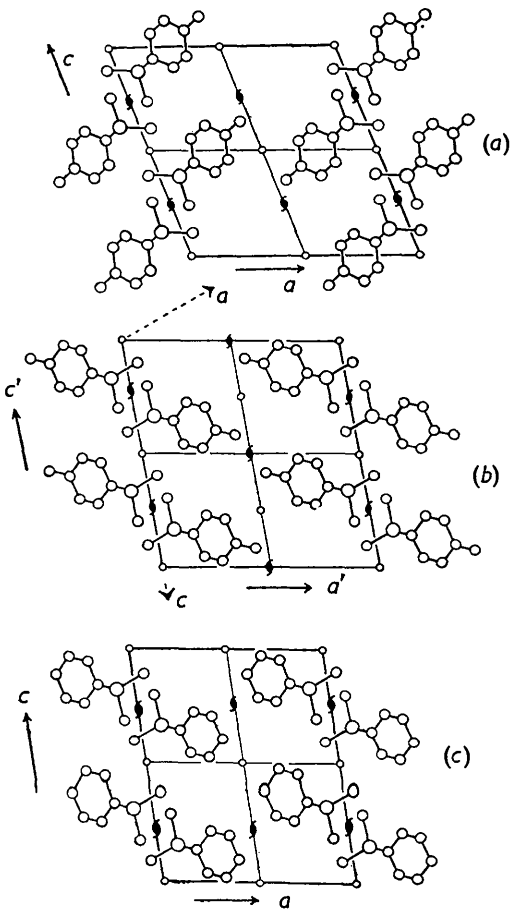

Fig. 3. (*a*) The structure of *p*-chlorobenzeneseleninic acid projected on (010). (*b*) The structure of *p*-chlorobenzeneseleninic acid with new choice of *a* axis to more clearly indicate relationship to the structure of benzeneseleninic acid. (*c*) The structure of benzeneseleninic acid. Note that when the projected structures are made to superimpose, the arrangement of symmetry elements is different.

Table 4. *Comparison of transformed* ($P2_1/n$) *cells of* para-*substituted acids with original* ($P2_1/c$) *cell of unsubstituted acid*

Acid	a (Å)	b (Å)	c (Å)	β
Benzeneseleninic	10·29	5·14	12·63	99° 15′
p-Tolueneseleninic	11·58	5·14	12·52	98° 30′
p-Chlorobenzeneseleninic	11·49	5·14	12·55	99° 35′
p-Nitrobenzeneseleninic	11·36	5·14	12·66	96° 45′

1. The lengths of the b axes of the two cells are identical within experimental error.
2. The observed y parameters for selenium are 0·9979 (σ = 0·0003) and 0·9969 (σ = 0·0029) in the unsubstituted acid and the *p*-chloro acid respectively.
3. The angle made by the Se–C_4 line and (010) in the unsubstituted acid is 47·2°, while the angle made by the Se–Cl line and (010) in the *p*-chloro acid is 46·5°.

Table 5. *Comparison of observed distances in p-chlorobenzeneseleninic acid with those in benzeneseleninic acid*

	p-Chloro acid		Unsubstituted acid	
Bonded	Length (Å)	σ (Å)	Length (Å)	σ (Å)
Se–C_1	1·85	0·07	1·903	0·021
Se–O_1	1·70	0·05	1·707	0·015
Se–O_2	1·79	0·05	1·765	0·015
C_4–Cl	1·69	0·08	—	—
Non-bonded				
Se–Se′	4·11	0·02	4·12	0·01
Se–Cl	6·42	0·04	(across benzene ring)	
Cl–Cl	4·14	0·06	(across center of symmetry)	
Cl–Cl	3·69	0·06	(along screw axis)	

4. When projections of the two acids on their respective (010) planes are drawn to the same scale and

Table 6. *Observed and calculated structure factors for p-chlorobenzeneseleninic acid*

Before the structure factors for the non-observed reflections could be calculated, SWAC was dismantled for an indefinite period, probably for several months. The F_c values given in Table 6 for the non-observed $h0l$ reflections are those computed earlier for parameter Set A. No values are available for the non-observed $hk0$ reflections. However, most of these are reflections for which k is odd. The selenium contribution is practically zero for these reflections and the calculated structure factors would be expected to be relatively small.

The F_o listed for the non-observed reflections are given as a single digit which represents the upper limit of the value.

$h\,k\,l$	F_o	F_c
$\overline{15}$,0,2	22·8	−18·7
4	12·6	14·5
6	29·1	30·7
8	19·0	−11·9
$\overline{14}$,0,2	17·7	−15·1
4	5	− 1·0
6	26·6	23·6
8	6·3	8·4
10	26·6	−26·0
$\overline{13}$,0,2	46·3	−50·1
4	26·0	−23·0
6	44·4	33·3
8	42·5	35·8
10	27·9	−23·0
12	15·2	−16·1
$\overline{12}$,0,2	8·8	−15·9
4	23·4	−24·6
6	6	−10·1
8	36·1	34·1
10	6	3·2
12	26·0	−25·1
14	6·9	− 9·8
$\overline{11}$,0,2	12·6	9·7
4	41·2	−38·4
6	22·8	−19·0
8	37·4	39·5
10	6	− 2·6
12	25·3	−24·6
14	17·7	−17·2
$\overline{10}$,0,2	34·2	32·5
4	7	− 2·4
6	48·2	−43·9
8	8·8	14·9
10	34·2	32·5
12	6	3·8
14	20·3	−29·1
$\overline{9}$ 0 2	69·7	62·0
4	7	16·0
6	46·3	−52·3
8	6	10·8
10	34·8	33·4
12	6	− 6·5
14	22·2	−27·3
$\overline{8}$ 0 2	56·4	54·6
4	29·1	40·4
6	51·3	−55·1
8	46·3	−42·5
10	69·1	61·3
12	41·2	40·7
14	28·5	−32·8
$\overline{7}$ 0 2	69·1	79·3
4	19·0	18·0
6	57·7	−47·7
8	53·2	−38·8
10	48·2	44·8
12	35·5	35·9
14	10·1	− 8·3
16	17·7	−24·9
$\overline{6}$ 0 2	30·4	29·5
4	106·5	95·8
6	20·9	21·8
8	144·6	−109·5
10	28·5	−26·7
12	35·5	35·8
14	15·2	17·5
16	15·2	−20·2
$\overline{5}$ 0 2	54·5	56·8
4	74·8	67·4
6	22·8	16·9
8	83·0	−64·6
10	15·8	−15·3
12	17·7	18·7
14	17·7	22·0
16	10·7	−14·1
$\overline{4}$ 0 2	87·5	−91·7
4	4	1·8
6	97·0	90·9
8	29·1	−26·0
10	39·3	−35·9
12	15·2	15·7
14	25·3	28·0
16	6·3	− 9·6
$\overline{3}$ 0 2	41·2	−49·2
4	12·6	−10·3
6	46·9	42·3
8	19·0	15·6
10	32·9	−30·4
12	17·7	−19·4
14	20·9	19·4
$\overline{2}$ 0 2	130·6	−190·4
4	86·2	−73·1
6	110·3	102·0
8	81·1	69·7
10	47·5	−46·1
12	25·3	−24·7
14	20·3	21·8
$\overline{1}$ 0 2	49·4	−51·3
4	65·3	−64·7
6	23·4	−23·1
8	69·7	60·5
10	6	6·2
12	34·8	−31·8
14	6·3	− 8·3
0 0 2	43·1	41·4
4	163·0	−157·8
6	48·8	−47·6
8	84·3	82·5
10	6	− 5·0
12	40·6	−42·1
14	10·7	− 8·9
1 0 0	47·5	85·4
2	12·6	12·0
4	28·5	−29·9
6	51·3	−53·5
8	47·5	44·0
10	34·8	34·4
12	6	1·8
14	21·5	−20·6
2 0 0	50·1	57·5
2	56·4	71·4
4	47·5	−51·2

Table 6 (*cont.*)

h k l	F_o	F_c
2 0 6	54·5	−57·0
8	50·1	43·7
10	29·1	32·5
12	6	− 9·3
14	24·1	−19·0
3 0 0	6·3	− 3·8
2	50·1	54·8
4	23·4	25·3
6	41·2	−44·2
8	22·2	−21·0
10	29·8	27·9
12	12·6	12·3
4 0 0	38·0	−40·9
2	62·8	72·6
4	6·3	3·2
6	36·7	−34·4
8	12·6	−10·3
10	20·3	17·4
12	8·8	7·6
5 0 0	74·2	−90·1
2	5	0·8
4	57·7	60·0
6	12·6	18·2
8	58·3	−57·8
10	15·8	−16·1
12	26·6	21·3
6 0 0	83·7	−89·8
2	22·8	19·0
4	44·4	42·3
6	6	3·1
8	33·6	−27·9
10	6·3	− 5·8
7 0 0	65·9	−62·8
2	86·2	−77·1
4	15·2	18·5
6	58·3	66·2
8	6	− 0·9
10	22·8	−20·6
8 0 0	43·7	−46·4
2	46·3	−36·6
4	15·2	15·9
6	28·5	28·1
8	6	− 7·0
9 0 0	27·9	23·9
2	48·8	−48·7
4	15·2	−19·4
6	36·1	28·0
8	6·3	4·5
10,0,0	12·6	7·6
2	24·7	−23·9
4	10·7	− 8·0
6	8·8	2·9
11,0,0	62·8	54·2
2	6	− 6·2
4	16·4	−22·2
6	4	− 2·3
12,0,0	15·2	13·7
2	6	5·8
4	4	2·8
13,0,0	6·3	7·6
2	22·2	18·8
14,0,0	4	− 0·9
0 2 0	106·0	110·4
4	29·2	26·5
6	16·0	15·9
1 2 0	76·8	70·3
3	25·6	21·0
4	60·7	58·9
6	24·1	31·4
2 1 0	59·2	−48·9
2	56·3	57·2
3	17·5	−15·3
4	16·0	10·4
3 1 0	68·0	68·4
3	25·6	26·7
4 1 0	26·3	26·3
2	45·3	−52·0
3	10·9	−16·0
4	44·6	−34·8
6	13·1	−14·9
5 1 0	16·0	14·4
2	82·6	−91·3
3	13·1	16·6
4	45·3	−38·4
6	16·0	−13·9
6 1 0	10·9	−13·2
2	76·8	−74·2
3	10·9	−13·6
4	45·3	−33·1
7 1 0	13·1	19·8
2	28·5	−29·0
3	16·0	22·6
4	31·4	−30·9
8 2 0	16·0	−15·0
3	10·9	−13·8
9 1 0	16·0	14·1
2	16·0	14·7
10,2,0	21·9	20·7
4	27·7	29·0
11,2,0	42·4	34·5
4	10·9	13·5
12,2,0	26·3	25·7
13,2,0	13·1	18·2

superimposed, the projections of the two molecules (omitting chlorine) are congruent within experimental error.

The final *y* parameters for carbon and oxygen atoms given in Set *C* are accordingly those from the unsubstituted acid already listed under Set *A*. The least-squares values for carbon and oxygen are listed in Set *B* for comparison, but they lead to a somewhat distorted benzene ring.

Discussion of the structure

The molecular structure of *p*-chlorobenzeneseleninic acid and the structure of the chains along the twofold screw axes are identical, within experimental error, to the corresponding features of the unsubstituted acid. The packing of the chains is, however, quite different in the two acids. The similarities and differences are shown in Fig. 3. When both crystals are set up as $P2_1/c$ (Fig. 3(*a*) and (*c*)), the structures appear quite different. On the other hand, if one takes a new *a* axis in the *p*-chloro acid such that the space group becomes $P2_1/n$, it becomes evident that the principal difference between the two structures is the interchange of symmetry centers with twofold screw axes located between the columns or chains. The constants for the new ($P2_1/n$) cells for the *para*-substituted acids are compared with those of unsubstituted acid in Table 4. Note that the space groups are not now the same, although the similarities in the cell constants strongly suggest isomorphism.

As indicated earlier, the details of the molecular structure are not as accurately determined in the present study as they were in the study of benzeneseleninic acid. The more significant distances in the *p*-chloro acid are shown in Table 5 together with the corresponding distances in the unsubstituted acid. Both the Se–C_1 and the C_4–Cl distances observed are shorter than the sum of the single-bond radii. However, owing to the large standard deviations involved, the difference is of doubtful significance. The observed Se–Cl distance (across the ring) of 6·42 Å compares favorably with the two crystallographically different Se–Cl distances in *p,p*′-dichlorodiphenyl diselenide of 6·41 and 6·39 Å (Kruse, Marsh & McCullough, 1953 and unpublished results.) The observed Se–Cl distance, although shorter than the calculated value of 6·48 Å based on the assumption of a normal benzene ring and single covalent bonds to the ring, is still long enough to suggest that the short observed Se–C_1 and C_4–Cl distances are not significant. If the latter observed distances are added to 2·78 Å, the normal C–C distance across a benzene ring, the result is only 6·32 Å. The observed Se–Cl distance of 6·42 Å, with its standard deviation of 0·04 Å, is probably significantly greater than 6·32 Å and less than 6·48 Å. The conclusion drawn, then, is that the Se–C_1 and C_4–Cl distances in *p*-chlorobenzeneseleninic acid are shorter than normal single covalent bonds, but not as short as the values listed in Table 5.

Comparison of the observed *F* values for the *h*0*l* and *hk*0 reflections with the calculated *F* values based on the atomic parameters in Set *C* of Table 2 is given in Table 6.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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Structure de $GeUO_4$.

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Préparé par chauffage à 1050° C. à l'abri de l'air d'un mélange équimoléculaire de GeO_2 et de UO_2 le germanate d'uranium, $GeUO_4$, s'apparente à la série des germanates $GeMO_4$ (M = Zr, Ce, Th) précédemment décrite (Bertaut & Durif, 1954).

Le diagramme Debye–Scherrer du produit obtenu correspond à une maille quadratique du type scheelite:

$$a = 5{\cdot}084,\ c = 11{\cdot}226\ \text{Å};\ Z = 4;$$
$$U = 290\ \text{Å}^3;\ D_X = 8{\cdot}49;\ I4_1/a\text{–}C^6_{4h}\ ,$$

avec:

$$\begin{array}{lll} & & +(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \\ 4\ \text{Ge} & \text{en}\ 4(a): & 0, 0, 0;\ 0, \tfrac{1}{2}, \tfrac{1}{4}; \\ 4\ \text{U} & \text{en}\ 4(b): & 0, 0, \tfrac{1}{2};\ 0, \tfrac{1}{2}, \tfrac{3}{4}; \\ 16\ \text{O} & \text{en}\ 16(f): & x, y, z;\ \bar{x}, \bar{y}, z; \\ & & \bar{y}, x, \bar{z};\ y, \bar{x}, \bar{z}; \\ & & x, \tfrac{1}{2}+y, \tfrac{1}{4}-z;\ \bar{x}, \tfrac{1}{2}-y, \tfrac{1}{4}-z; \\ & & y, \tfrac{1}{2}-x, \tfrac{1}{4}+z;\ y, \tfrac{1}{2}-x, \tfrac{1}{4}+z\ . \end{array}$$

Les paramètres de position de l'oxygène sont difficilement accessibles à la mesure à cause de la présence de l'atome lourd d'uranium. Des considérations stériques permettent de les estimer très voisins des valeurs:

$$x = 0{\cdot}27,\ y = 0{\cdot}11,\ z = 0{\cdot}08\ ,$$

qui conduisent aux distances interatomiques suivantes:

$$\begin{array}{lll} \text{O–O}_\text{I} = 2{\cdot}97\ \text{Å}, & \text{U–O}_\text{I} = 2{\cdot}31\ \text{Å}, & \text{Ge–O} = 1{\cdot}74\ \text{Å}\ , \\ \text{O–O}_\text{II} = 2{\cdot}76\ \text{Å}, & \text{U–O}_\text{II} = 2{\cdot}47\ \text{Å}; & \end{array}$$

ajoutons que les distances généralement admises sont:

$$\text{Ge–O} = 1{\cdot}76\ \text{Å}\ \ \text{et}\ \ \text{U–O} = 2{\cdot}37\ \text{Å}\ (\text{dans}\ UO_2)\ .$$

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Référence

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