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The Crystal Structure of *p,p'*-Dichlorodiphenyl Diselenide and *p,p'*-Dichlorodiphenyl Ditelluride*

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Crystals of *p,p'*-dichlorodiphenyl diselenide and *p,p'*-dichlorodiphenyl ditelluride are isomorphous. The space group is $P2_1/n$ with four molecules in the unit cell. The structures were determined by use of two- and three-dimensional Fourier syntheses and least-squares refinements. The observed Se–Se and Te–Te bonded separations are 2·333±0·015 Å and 2·702±0·010 Å respectively, compared to single-bond radius sums of 2·34 Å and 2·74 Å. Other observed distances and bond angles are tabulated. All are consistent with the accepted values from earlier investigations.

Introduction

p,p'-Dichlorodiphenyl diselenide is an orange-colored crystalline solid melting at 90° C. The crystals are lath-shaped, monoclinic needles elongated on *b*. The principal faces are of the type (101) and there is a tendency toward twinning on the plane (001). Crystals suitable for X-ray diffraction work were grown by slow evaporation of solutions in ethanol. The ditelluride is a garnet-red crystalline solid melting at 117° C. The needle habit of growth is even more pronounced than in the diselenide, and twinning so common that finding suitable single crystals was difficult. Also the presence of oxygen and moisture in solvents caused considerable oxidation and hydrolysis, especially with alcohols, acetone and the like. The best single crystals were obtained by slow evaporation of solutions of the ditelluride in dry benzene under an atmosphere of dry nitrogen.

Intensity data

For the rotation and Weissenberg photographs about the *b* axis, needles were selected which had nearly uniform diameters of 0·15 mm. for the diselenide and 0·05 mm. for the ditelluride. Values of μR are thus approximately 0·80 and 0·75 respectively for Cu $K\alpha$ radiation, and no absorption corrections were considered necessary. For the photographs about the other axes it was necessary to cleave and shape the crystals by selective dissolution. Even so, the resulting fragments were not uniform in diameter. As a result, these photographs were undoubtedly subject to undesired absorption effects for which no correction was made. The intensity photographs were prepared by the multiple-film method and the intensities were estimated visually with the aid of standard comparison strips consisting of timed exposures on the same crystal. The intensities were corrected in the usual way to give sets of $|F_o|$ values.

Crystallographic data

The lattice constants and density data are given in Table 1. The only systematic absences are $h0l$ with $h+l$ odd and $0k0$ with k odd. The space group was accordingly taken to be $P2_1/n$. The approximate density of the diselenide of 1·9 g.cm.$^{-3}$, observed by flotation, indicates that there are four molecules of $(ClC_6H_4Se)_2$ in the unit cell. There is thus no required molecular symmetry.

Table 1. *Crystallographic data for p,p'-dichlorodiphenyl diselenide and p,p'-dichlorodiphenyl ditelluride*

Cu $K\alpha$ radiation, λ = 1·542 Å.

	Diselenide	Ditelluride
a (Å)	14·09±0·05	14·34±0·02
b (Å)	6·48±0·03	6·47±0·01
c (Å)	14·55±0·05	15·09±0·02
β (°)	102·8 ±0·2	101·5 ±0·5
d_o (g.cm.$^{-3}$)	1·9	—
Z	4	4
d_c (g.cm.$^{-3}$)	1·967	2·329

Determination of the structure

The structure of the diselenide was determined first, and the ditelluride work was carried out by analogy with the diselenide. A Patterson summation on (010) served to determine the approximate x and z parameters of the two selenium and two chlorine atoms in the asymmetric unit. These atoms were then used to fix the signs of the $F(h0l)$ values and two successive Fourier syntheses on (010) were prepared. Approximate carbon positions were indicated in the first Fourier synthesis and inclusion of these in the prepa-

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Table 2. *Atomic positional parameters in p,p'-dichlorodiphenyl diselenide*

		Two-dimensional Fourier refinement	Three-dimensional Fourier refinement		Three-dimensional least-squares refinement		Final parameters with idealized carbon positions
			Corrected parameters	Backshift corrections	Final parameters	Standard deviation	
Se	x	0·448	0·447	−0·001	0·4458	0·0004	0·4458
	y	0·25	0·250	−0·005	0·2444	0·0011	0·2444
	z	0·414	0·413	0·000	0·4137	0·0003	0·4137
Se′	x	0·613	0·612	0·000	0·6123	0·0004	0·6123
	y	0·25	0·249	0·004	0·2534	0·0013	0·2534
	z	0·418	0·418	−0·001	0·4185	0·0003	0·4185
Cl	x	0·303	0·303	−0·001	0·3032	0·0010	0·3032
	y	0·85	0·848	−0·002	0·8445	0·0032	0·8445
	z	0·065	0·062	−0·004	0·0616	0·0009	0·0616
Cl′	x	0·617	0·618	0·000	0·6182	0·0011	0·6182
	y	0·67	0·678	0·010	0·6807	0·0026	0·6807
	z	0·064	0·063	−0·002	0·0625	0·0010	0·0625
C_1	x	0·405	0·402	0·008	0·396	0·004	0·402
	y	0·43	0·417	0·013	0·420	0·011	0·424
	z	0·312	0·311	0·007	0·312	0·004	0·307
C_2	x	0·331	0·334	0·000	0·338	0·004	0·339
	y	0·37	0·356	−0·024	0·315	0·011	0·352
	z	0·237	0·233	−0·007	0·231	0·004	0·226
C_3	x	0·299	0·302	0·004	0·307	0·004	0·308
	y	0·50	0·457	0·007	0·464	0·011	0·482
	z	0·161	0·157	−0·006	0·153	0·004	0·149
C_4	x	0·342	0·341	−0·010	0·337	0·004	0·340
	y	0·69	0·684	−0·019	0·695	0·011	0·686
	z	0·159	0·155	0·000	0·154	0·004	0·154
C_5	x	0·416	0·409	−0·012	0·400	0·004	0·403
	y	0·75	0·753	0·000	0·781	0·011	0·759
	z	0·233	0·235	−0·001	0·233	0·004	0·235
C_6	x	0·448	0·437	0·000	0·435	0·004	0·434
	y	0·62	0·612	0·012	0·620	0·011	0·629
	z	0·310	0·314	−0·008	0·316	0·004	0·311
C'_1	x	0·614	0·618	−0·003	0·618	0·004	0·614
	y	0·08	0·093	−0·025	0·081	0·011	0·082
	z	0·314	0·314	0·002	0·311	0·004	0·312
C'_2	x	0·572	0·587	−0·001	0·587	0·004	0·579
	y	0·15	0·177	0·001	0·164	0·011	0·157
	z	0·224	0·227	−0·004	0·233	0·004	0·221
C'_3	x	0·573	0·577	0·006	0·584	0·004	0·581
	y	0·02	0·028	0·000	0·031	0·011	0·032
	z	0·146	0·143	0·004	0·141	0·004	0·144
C'_4	x	0·616	0·612	0·002	0·615	0·004	0·617
	y	0·83	0·856	0·009	0·878	0·011	0·832
	z	0·159	0·154	0·002	0·154	0·004	0·157
C'_5	x	0·658	0·651	0·009	0·654	0·004	0·651
	y	0·76	0·762	−0·005	0·762	0·011	0·757
	z	0·249	0·249	−0·002	0·250	0·004	0·247
C'_6	x	0·657	0·661	0·001	0·656	0·004	0·650
	y	0·89	0·883	0·000	0·893	0·011	0·881
	z	0·327	0·328	−0·004	0·322	0·004	0·325

ration of the second synthesis resulted in positions leading to no further changes in sign. Unfortunately, the carbon atoms were not all resolved. Pairs of atoms C_1 and C_6, C_3 and C_4, C'_1 and C'_6, and C'_3 and C'_4 combined to yield elliptical peaks on the electron-density map. However, the assumptions that atoms C_1 and C_4 and C'_1 and C'_4 are in straight lines with their respective selenium and chlorine atoms and that the ring is a regular hexagon are sufficient to give tentative x and z parameters for the carbon atoms. These are listed in the first column of Table 2.

Attention was then directed to summations on (100). An interesting feature of the $0kl$ data is the appearance of only one reflection, (013), with l odd, and this one with the weakest observable intensity under the conditions employed. Over 50 such planes were within range with the radiation and camera used, but long exposures showed no additional reflections with l odd. This indicates that a pseudo glide plane perpendicular to a and with a glide of $\frac{1}{2}d_{(001)}$ is present, a situation which would result if the y parameters of the atoms in a molecule were symmetrically distributed about $y = \frac{1}{4}$. The final structure shows approximately such a distribution and the resulting pseudo glide planes.

The Patterson synthesis on (100) showed only one prominent peak, that at $Y = 0{\cdot}50$, $Z = 0{\cdot}16$. This indicates that the selenium atoms are both at or near $y = 0{\cdot}25$ and are thus lined up in the direction of the a axis. No indication of the chlorine positions was in evidence and the Fourier synthesis on (100) served only to confirm the selenium positions. However, a possibility, which later proved to be the case, was that both chlorine atoms might be eclipsed by the two selenium atoms. It later developed that the two chlorine atoms fell within 0·5 Å of the position of the selenium atoms on this projection of the structure and were therefore unresolved by the Fourier synthesis.

Summations on (001) were of little help in locating the chlorine atoms. This was due in part to the difficulty, because of the crystal habit, of preparing good intensity photographs about the c axis and in part to the fortuitous y parameter of 0·25 for the two selenium atoms. This latter circumstance made it difficult to assign phases to the $F(hk0)$ values for which h is odd, for, in this case, the selenium contribution is zero.

Because of the above situation, a partial three-dimensional Patterson summation was undertaken. For this summation, which consisted of lines through Patterson space parallel to the b axis, first-, second- and third-layer Weissenberg photographs about the b axis were combined with the zero-layer data previously used. The summation was carried out along lines through $X = 0{\cdot}145$, $Z = 0{\cdot}358$ (corresponding to interaction between Se and Cl); $X = 0$, $Z = 0{\cdot}358$ (corresponding to interaction between Se′ and Cl′); and $X = 0{\cdot}307$, $Z = 0$ (corresponding to interaction between Cl and Cl′). Maxima were found at $Y = \pm 0{\cdot}46$, $Y = \pm 0{\cdot}43$ and $Y = \pm 0{\cdot}17$ respectively. A set of y parameters consistent with these maxima and the general absence of $0kl$ with l odd (requiring that the y parameters be distributed in an approximately symmetrical manner about $y = \frac{1}{4}$) is given in the first column of Table 2. The y parameters for carbon are again based on the assumption of regular hexagons for the phenyl groups.

It is of interest to note at this point the close similarity between what is reported here as the correct structure (Structure B) and a presumably incorrect structure (Structure A). Both structures give identical projections on (010) if the positions of the symmetry elements are ignored: they are related by interchange of the positions of the 2_1 screw axis and the symmetry centers in the projection. Structure A was the one first assumed to be correct, but the relatively large value of $R = 0{\cdot}32$ for the $hk0$ reflections caused some concern. Of especial concern was the fact that the 36 reflections for which h is even had an R of 0·20 while the 15 reflections for which h is odd had an R of 0·83. Five of the latter reflections were off by more than a factor of 5, a fact which is especially significant. When Structure B was considered as a possibility, the difficulty was resolved, as shown in Table 3, in which values of R for Structures A and B at this stage of refinement are compared. Also included for comparison are the values of R for Structure B after three-dimensional refinement.

Table 3. *Comparison of values of R for Structures A and B after two-dimensional refinement*

Isotropic temperature factor of 3·95 Å² used

	$h0l$	$0kl$	$hk0$
Number of reflections observed	131	52	51
Structure A	0·13	0·14	0·32
Structure B	0·13	0·14	0·25
Structure B after three-dimensional refinement	0·108	0·132	0·180

The two structures (A and B) involve the same molecular structure and the only feature of the packing in the incorrect structure which would cause comment is a packing separation of 3·2 Å between two chlorine atoms. The accepted van der Waals radius for chlorine would indicate a minimum separation of 3·6 Å. In Structure B, the minimum non-bonded Cl–Cl approach is 3·85 Å.

Refinement of the structure

On the assumption that Structure B was the correct trial structure, three-dimensional Fourier syntheses were prepared by use of SWAC (Sparks, Prosen, Kruse & Trueblood, 1956). For this purpose the 550 F_o values in Table 5 were employed. These include complete data from the equator and first three layer lines about the b axis plus the $hk0$ and $0kl$ data. Although approximately 1700 reflections are possible with Cu $K\alpha$ radiation, an unusually high fraction of these are not observed because of the pseudo-symmetry of the structure.

Table 4. *Anisotropic temperature factors*

(Values in Å²)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Se	4·2	3·5	2·9	−1·3	4·1	−0·6
Se′	4·0	4·7	3·3	1·8	−0·1	2·7
Cl	3·4	8·7	3·5	1·4	1·8	−2·0
Cl′	5·8	2·5	4·2	0·1	2·3	−1·0
C*	3·1	3·9	4·8	0·8	3·0	0·8
C†	—	—	—	10·9	8·1	8·4

* Average. † Average of absolute magnitudes.

Table 5. *Comparison of observed and calculated structure factors in p,p'-dichlorodiphenyl diselenide*

h k l	F_o	F_c
00 00 02	30	40
00 00 04	105	106-
00 00 06	191	192-
00 00 08	138	125-
00 00 10	<22	14-
00 00 12	91	91
00 00 14	38	40
00 00 16	<17	3-
00 00 18	16	24-
01 00 01	113	122
01 00 03	<13	8
01 00 05	88	90-
01 00 07	86	108-
01 00 09	<22	3-
01 00 11	97	94
01 00 13	38	30
01 00 15	<20	0
01 00 17	<19	20
01 00 01-	111	112
01 00 03-	44	43-
01 00 05-	119	118-
01 00 07-	83	89-
01 00 09-	44	39
01 00 11-	172	108
01 00 13-	27	18
01 00 15-	<22	14
01 00 17-	27	38-
02 00 00	55	75
02 00 02	36	40
02 00 04	30	29-
02 00 06	44	53-
02 00 08	22	23-
02 00 10	27	31
02 00 12	<25	22-
02 00 14	<25	19
02 00 16	<20	14
02 00 02-	<13	8-
02 00 04-	52	66-
02 00 06-	63	83-
02 00 08-	<20	2-
02 00 10-	66	67
02 00 12-	44	46
02 00 14-	<24	11-
02 00 16-	<20	19
02 00 18-	16	25-
03 00 01	136	129
03 00 03	91	68
03 00 05	<17	6
03 00 07	<20	6
03 00 09	24	18-
03 00 11	55	55-
03 00 13	<25	6-
03 00 15	<23	8-
03 00 01-	44	40
03 00 03-	80	81-
03 00 05-	61	63-
03 00 07-	58	50-
03 00 09-	30	31-
03 00 11-	<25	27
03 00 13-	66	57
03 00 15-	<25	3
03 00 17-	<20	0
04 00 00	180	228-
04 00 02	149	148-
04 00 04	22	20-
04 00 06	36	29
04 00 08	66	64
04 00 10	38	40
04 00 12	<25	19-
04 00 14	27	27-
04 00 02-	194	183
04 00 04-	55	62
04 00 06-	77	79
04 00 08-	22	21
04 00 10-	36	38-
04 00 12-	52	49-
04 00 14-	<25	0
04 00 16-	<20	5
05 00 01	174	173-
05 00 03	99	112-
05 00 05	<20	3
05 00 07	86	88
05 00 09	83	91
05 00 11	27	18-
05 00 13	36	44-
05 00 15	<20	19-
05 00 03-	138	129
05 00 05-	97	123
05 00 07-	33	36
05 00 09-	66	75-
05 00 11-	74	71-
05 00 13-	<25	8
05 00 15-	<22	17-
05 00 17-	22	23
06 00 00	65	73-
06 00 02	94	96-
06 00 04	22	20-
06 00 06	66	74
06 00 08	105	97
06 00 10	<24	8
06 00 12	36	45-
06 00 14	38	46-
06 00 02-	55	46
06 00 04-	77	98
06 00 06-	27	31
06 00 08-	66	81-
06 00 10-	94	77-
06 00 12-	<25	20-
06 00 14-	36	41
06 00 16-	33	33
07 00 01	108	109-
07 00 03	155	144-
07 00 05	41	45-
07 00 07	47	37
07 00 09	55	50
07 00 11	<25	25-
07 00 13	<22	2-
07 00 15	16	27-
07 00 01-	86	82
07 00 03-	166	171
07 00 05-	80	97
07 00 07-	<20	20-
07 00 09-	97	87-
07 00 11-	83	85-
07 00 13-	<24	14-
07 00 15-	49	52
08 00 00	18	19-
08 00 02	27	27-
08 00 04	66	59-
08 00 06	<25	6-
08 00 08	36	31
08 00 10	27	24
08 00 12	<22	2-
08 00 14	<18	8
08 00 02-	33	28
08 00 04-	83	96
08 00 06-	<22	9-
08 00 08-	69	56-
08 00 10-	30	36-
08 00 12-	<25	0
08 00 14-	<24	22-
08 00 16-	24	27
09 00 01	<23	0
09 00 03	<24	8
09 00 05	<25	27-
09 00 07	<25	19
09 00 09	<24	5-
09 00 11	24	13-
09 00 01	44	41-
09 00 03-	24	25-
09 00 05-	<22	10-
09 00 07-	<23	5
09 00 09-	<24	22
09 00 11-	<24	17-
09 00 13-	<24	10
09 00 15-	<23	5-
10 00 00	21	20
10 00 02	36	37
10 00 04	<23	14-
10 00 06	<23	10-
10 00 08	38	44-
10 00 10	27	28-
11 00 01	<23	7-
11 00 03	58	63
11 00 05	30	33
11 00 07	<23	7-
11 00 09	33	35-
11 00 11	22	15-
11 00 01-	74	65-
11 00 03-	58	45-
11 00 05-	<23	2-
11 00 07-	38	42
11 00 09-	38	45
11 00 11-	<23	2
11 00 13-	27	35-
12 00 00	38	36-
12 00 02	<23	0
12 00 04	55	66
12 00 06	30	35
12 00 08	<22	2
12 00 10	27	31-
12 00 02-	86	99-
12 00 04-	33	24-
12 00 06-	38	36
12 00 08-	77	80
12 00 10-	<23	15-
12 00 12-	<23	22-
12 00 14-	24	27-
13 00 01	<22	0
13 00 03	30	33
13 00 05	30	31
13 00 07	<22	2
13 00 01-	36	25-
13 00 03-	36	35-
13 00 05-	<22	10
13 00 07-	38	31
13 00 09-	<22	5
00 01 01	<9	1
00 01 02	181	274
00 01 03	8	5-
00 01 04	170	253
00 01 05	<15	4-
00 01 06	26	30
00 01 07	<18	1
00 01 08	103	105-
00 01 09	<20	2
00 01 10	120	114-
00 01 11	<22	2
00 01 12	21	24-
00 01 13	<24	4-
00 01 14	48	39
00 01 15	<24	4-
00 01 16	38	36
01 01 00	8	11-
01 01 01	36	47
01 01 02	<15	16
01 01 03	111	133
01 01 04	15	13-
01 01 05	54	67
01 01 06	39	37-
01 01 07	58	62-
01 01 08	<20	1-
01 01 09	102	88-
01 01 10	27	16
01 01 11	28	22-
01 01 12	<21	0
01 01 13	31	29
01 01 14	<23	9-
01 01 15	39	41
01 01 01-	64	87-
01 01 02-	14	19
01 01 03-	103	146-
01 01 04-	32	45
01 01 05-	31	32-
01 01 06-	40	31
01 01 07-	101	103
01 01 08-	<22	19-
01 01 09-	108	100
01 01 10-	<22	17-
01 01 11-	<22	2-
01 01 12-	<22	1-
01 01 13-	54	50-
01 01 14-	<20	15-
01 01 15-	39	46-
02 01 00	39	21-
02 01 01	75	74-
02 01 02	51	58
02 01 03	15	4
02 01 04	66	56
02 01 05	108	77
02 01 06	<19	1-
02 01 07	<20	3-
02 01 08	35	45-
02 01 09	<22	1-
02 01 10	35	30-
02 01 01-	82	71
02 01 02-	65	67-
02 01 03-	105	94-
02 01 04-	40	48-
02 01 05-	47	44-
02 01 06-	46	41
02 01 07-	58	27
02 01 08-	73	69
02 01 09-	<22	9-
02 01 10-	28	26
03 01 01	<17	5-
03 01 02	<18	3-
03 01 03	16	28
03 01 04	35	19
03 01 05	40	38
03 01 06	<21	15-
03 01 07	43	36
03 01 08	<21	12-
03 01 09	56	37
03 01 01-	105	90-
03 01 02-	<18	28-
03 01 03-	81	88-
03 01 04-	25	14-
03 01 05-	18	10-
03 01 06-	31	30
03 01 07-	<20	21-
03 01 08-	<20	18-
03 01 09-	56	51
03 01 10-	<22	8-
03 01 11-	38	37
04 01 00	49	75
04 01 01	<18	5-
04 01 02	<18	1-
04 01 03	<19	9-
04 01 04	117	118-
04 01 05	<20	16-
04 01 06	66	69-
04 01 07	<23	23-
04 01 08	<23	14-
04 01 09	<22	1-
04 01 10	58	51
04 01 01-	15	25
04 01 02-	171	184
04 01 03-	18	28
04 01 04-	<20	10-
04 01 05-	21	7
04 01 06-	34	38-
04 01 07-	<18	16-
04 01 08-	68	67-
04 01 09-	<22	25-
04 01 10-	36	32-
05 01 00	6	10-
05 01 01	67	65
05 01 02	19	20-
05 01 03	82	73-
05 01 04	<19	0
05 01 05	104	127-
05 01 06	25	23
05 01 07	53	52-
05 01 08	<22	23-
05 01 09	70	59
05 01 10	<21	1-
05 01 11	61	54
05 01 01-	139	159
05 01 02-	61	48-
05 01 03-	99	104
05 01 04-	25	20-
05 01 05-	63	58-
05 01 06-	29	18
05 01 07-	123	111-
05 01 08-	44	36
05 01 09-	49	50-
05 01 10-	<21	5-
05 01 11-	28	22
05 01 12-	<20	9-
05 01 13-	61	49
06 01 00	81	76
06 01 01	<19	4-
06 01 02	23	23-
06 01 03	39	34
06 01 04	106	101-
06 01 05	<22	13-
06 01 06	84	80-
06 01 07	<22	6-
06 01 08	<22	25-
06 01 09	<21	5-
06 01 10	66	72
06 01 11	<21	0
06 01 12	39	41
06 01 01-	27	21-
06 01 02-	87	92
06 01 03-	66	41
06 01 04-	<19	23-
06 01 05-	24	18-
06 01 06-	91	85-
06 01 07-	24	18-
06 01 08-	68	61-
06 01 09-	<22	3-
06 01 10-	32	34
06 01 11-	<21	0
06 01 12-	66	64
06 01 13-	<20	3-
06 01 14-	31	32
07 01 00	7	19
07 01 01	119	111
07 01 02	22	18
07 01 03	<21	12-
07 01 04	<22	2-
07 01 05	107	88-
07 01 06	<22	12-
07 01 07	55	57-
07 01 08	<21	0
07 01 09	<20	15-
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07 05 00	17	25
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05 06 00	<14	3-
06 06 00	18	21
07 06 00	<13	4
08 06 00	<12	1-
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00 07 03	<16	8-
00 07 04	21	15-
00 07 05	<13	4
00 07 06	<13	10-
00 07 07	<12	2-
00 07 08	28	27

The F_o synthesis showed well-resolved maxima for all atoms other than hydrogen. The positions of the maxima were located by means of the 19-point routine on SWAC. A set of structure factors was then computed which included the isotropic temperature factor $B = 3{\cdot}95$ Å^2. A few phase changes were involved and a second F_o synthesis and set of structure factors were computed. These structure factors were used in the preparation of a three-dimensional F_c synthesis by use of which the backshift corrections listed in

Table 2 were computed. Application of these backshift corrections gave the positional parameters in the second column of Table 2. The value of R for the 550 observed reflections then became 0·157 when the above isotropic temperature factor was used.

The incompleteness of the intensity data, as well as inaccuracies due to unevaluated absorption effects, probably made further refinement of the structure unjustified. However, it was desired to use this structure as one of the test cases for the newly coded least-squares refinement routine on SWAC (Sparks *et al.*, 1956). In all, eight least-squares cycles were carried out. Here also, the large number of cycles was unjustified except for the computing experience gained. On the first cycle, the average parameter shifts were 0·0009 for Se, 0·0005 for Cl and 0·003 for C. The average shifts had reduced to 0·0002, 0·0003 and 0·0009 respectively on the last cycle. The resulting atomic parameters, with their standard deviations from the least-squares refinement, are given in the third column of Table 2.

Since the routine provides for individual anisotropic temperature factors, these were included in the least-squares refinement. The temperature factor applied to each atom is of the type

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right] .$$

Change in orientation of the ellipsoid from one equivalent position to another is provided for in the routine (Trueblood, 1956). The final values of the vibrational parameters are given in Table 4. The values for selenium and the B_{11} and B_{33} values for chlorine are of possible significance, but the values for carbon and the B_{22} values for chlorine are probably not. The positional and vibrational parameters for carbon are naturally most affected by inaccuracies in the intensity data.

It should be pointed out that the values of the cross terms B_{ij} for many of the individual carbon atoms must be regarded as mathematical artifacts; in a physical sense, they can have no meaning. Thus, it can be easily shown that, for a real atom, the maximum permissible magnitude for any B_{ij} is equal to $2\sqrt{(B_{ii}B_{jj})}$; if $B_{ij}^2 > 4B_{ii}B_{jj}$, the implied thermal motion becomes hyperbolic rather than elliptical, with imaginary components in the directions perpendicular to the axis of the hyperbola. In reciprocal space, this situation requires that, for certain planes hkl, the effective atomic form factor be greater than that corresponding to a stationary atom.

It has been of interest also to compute a set of idealized carbon parameters. These were obtained by assuming a regular planar hexagon 1·39 Å on an edge located in the mean plane of the least-squares parameters. The Se–C_1–C_4–Cl lines were assumed straight and the C_4–Cl distance was taken as 1·69 Å, the value found most frequently in other chlorobenzene compounds (Pauling, 1945, p. 215). The parameters in the last column of Table 2 are made up of the least-squares values for selenium and chlorine and the idealized parameters for carbon. The F_c values in Table 5 are based on the final positional parameters in Table 2 and the vibrational parameters in Table 4. Average vibrational parameters were used for carbon since the individual values ranged from 0·6 to 16 for B_{ii} and those of B_{ij} varied from −28 to 49. The final value for R for all observed reflections is 0·136. It is interesting to note that the least-squares refinement caused only three phase changes in the 550 structure factors, and these in very weak reflections.

Discussion of the structure

The molecular structure and packing arrangement in *p,p'*-dichlorodiphenyl diselenide are shown in Fig. 1. With the possible exception of the dihedral angle along the Se–Se bond, the molecular structure found conforms with expectations. Bonded separations, bond angles and packing distances are given in Tables 6, 7 and 8. The Se–Se bonded distance of 2·33 Å compares favorably with the value 2·34 Å found in α-selenium (Burbank, 1951), and β-selenium, (Marsh, Pauling & McCullough, 1953), the value 2·33 Å found in selenium diselenocyanate (Aksnes & Foss, 1954) and the value 2·32 Å found in hexagonal selenium (Bradley, 1924). It is slightly larger than the value 2·29 Å found in diphenyl diselenide (Marsh, 1952).

It is unfortunate that the uncertainties in the carbon positions (σ = 0·1 Å) do not permit the direct cal-

Table 6. *Intramolecular distances in p,p'-dichlorodiphenyl diselenide*

	Three-dimensional Fourier	Three-dimensional least squares	Standard deviation	Final parameters
Se–Se'	2·31 Å	2·333 Å	0·015 Å	2·333 Å
Se–Cl	6·39	6·41	0·03	6·41
Se'–Cl'	6·37	6·39	0·03	6·39
Se–C_1	1·84	1·88	0·10	1·94
Se'–C_1'	1·84	1·93	0·10	1·92
Cl–C_4	1·71	1·65	0·11	1·69*
Cl'–C_4'	1·77	1·86	0·11	1·69*
C–C(Ave.)	1·41	1·40	0·14†	1·39*
C–C(Max.)	1·58	1·59	0·18†	1·39*
C–C(Min.)	1·22	1·09	0·12†	1·39*

* Required by conditions imposed on idealized carbon parameters.

† Individual value. Does not necessarily apply to bond distance in same row.

Table 7. *Bond angles in p,p'-dichlorodiphenyl diselenide*

	Three-dimensional Fourier	Three-dimensional least squares
Se'–Se–Cl	101·5°	102·2°
Se–Se'–Cl'	101·4	100·0
C–C–C (Ave.)	119·8	119·9
C–C–C (Max.)	129	130
C–C–C (Min.)	116	109
Dihedral angle		
C_1SeSe'/SeSe'C_1'	—	74·5

Table 8. *Packing distances in p,p'-dichlorodiphenyl diselenide*

	Observed separation	Sum of van der Waals radii
Se–Se′	4·25 Å	4·00 Å
Se–Se	4·24	4·00
Se–Cl	3·66	3·80
Se′–Cl′	3·78	3·80
Cl–Cl′	3·85	3·60
C_2–C_5	3·61	3·70
C_2'–C_5'	3·64	3·70

culation of more reliable values for the Se–C and Cl–C distances. However, the Se–Cl distances across the rings of 6·41 Å and 6·39 Å (σ = 0·03 Å), together with the fairly well established Cl–C (aromatic) distance of 1·69 Å and the accepted structure of the benzene ring, lead to Se–C distances of 1·94 Å and 1·92 Å respectively. These values fall in the range of distances (1·91–1·95 Å), found in various diaryl selenides and their dihalides (McCullough & Hamburger, 1941; McCullough & Marsh, 1950; Blackmore & Abrahams, 1955*a*). The average value (1·93 Å) from the present study, also the median of the range of values previously reported, may accordingly be taken as fairly representative of the Se–C (aromatic) bond distance in diaryl diselenides, diaryl selenides and the dihalides of the latter. However, the Se–C (aromatic) bond distances of 1·903 Å (σ = 0·021) in benzeneseleninic acid (Bryden & McCullough, 1954) and of 1·85 Å (σ = 0·07) in *p*-chlorobenzeneseleninic acid (Bryden & McCullough, 1956) indicate that in these compounds of more highly oxidized selenium, the Se–C distance may be significantly shorter than in the diaryl selenides, etc. The Se–C (aliphatic) distance appears to be somewhat larger than the distances above. For example, the Se–C distance in 1,4-diselenane is 2·01±0·03 Å (Marsh & McCullough, 1951) and that in dimethylselenide is 1·977±0·012 Å (Goldish, Hedberg, Marsh & Schomaker, 1955). If one accepts a distance of 1·98 Å as being that of a normal single covalent Se–C bond, then the observed Se–C (aromatic) distance of 1·93 Å is short to approximately the same degree that the Cl–C (aromatic) distance of 1·69 Å is shorter than the radius sum, 1·76 Å, for a single covalent Cl–C bond. As pointed out by Goldish *et al.* (1955), the selenium radius for a normal, single covalent bond should probably be taken as 1·22 Å, rather than as 1·17 Å, the value which has been accepted for many years.

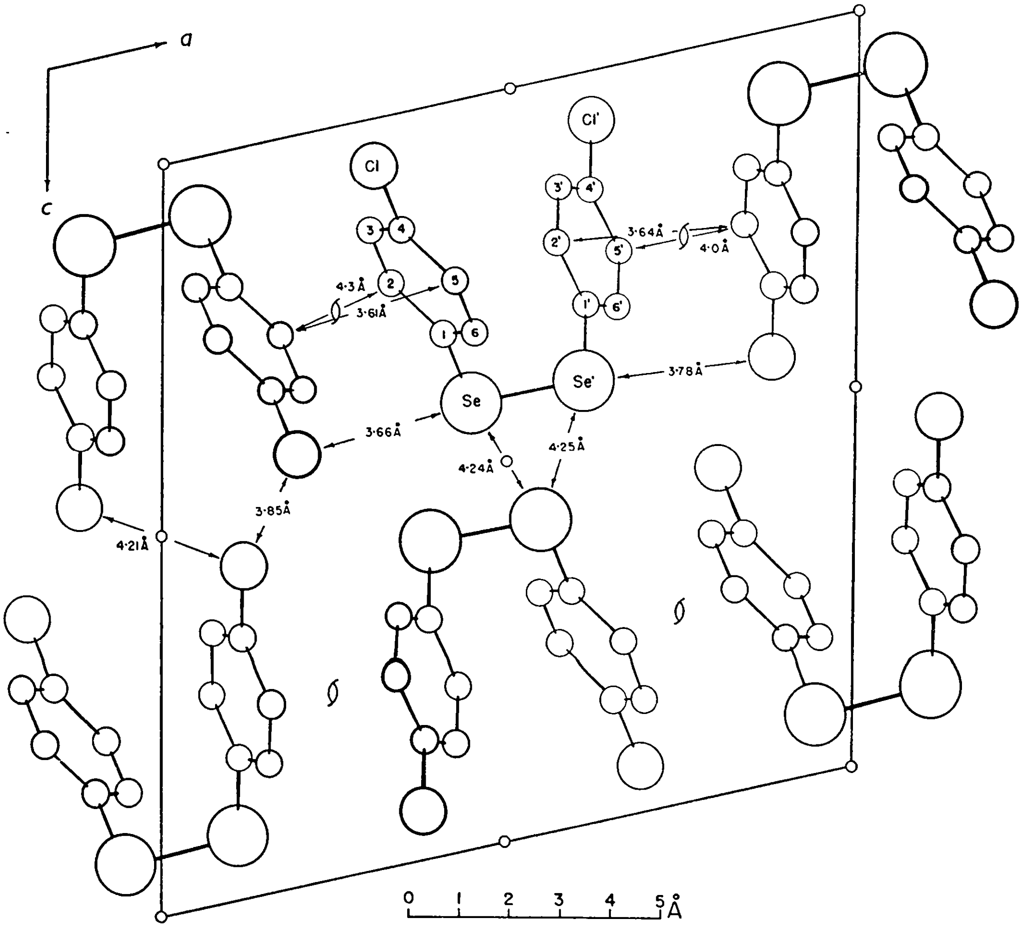

Fig. 1. The structure of p,p'-dichlorodiphenyl diselenide viewed down the b axis.

Table 9. *Atomic parameters in p,p′-dichlorodiphenyl ditelluride*

		Fourier refinement	Least-squares refinement	Standard deviation	Final parameters with idealized carbon positions
Te	x	0·432	0·4321	0·0003	0·4321
	y	0·247	0·239	0·005	0·239
	z	0·417	0·4161	0·0003	0·4161
Te′	x	0·618	0·6209	0·0003	0·6209
	y	0·258	0·260	0·005	0·260
	z	0·418	0·4203	0·0003	0·4203
Cl	x	0·318	0·3153	0·0010	0·3153
	y	0·850	0·863	0·015	0·863
	z	0·069	0·0670	0·0010	0·067
Cl′	x	0·616	0·6101	0·0010	0·6101
	y	0·685	0·674	0·015	0·674
	z	0·066	0·0658	0·0010	0·0658
C_1	x	0·396	0·398	0·006	0·393
	y	0·451	0·460	0·030	0·446
	z	0·302	0·307	0·006	0·297
C_2	x	0·326	0·323	0·006	0·326
	y	0·389	0·378	0·030	0·383
	z	0·234	0·225	0·006	0·226
C_3	x	0·300	0·298	0·006	0·302
	y	0·516	0·511	0·030	0·512
	z	0·149	0·141	0·006	0·152
C_4	x	0·350	0·338	0·006	0·345
	y	0·685	0·663	0·030	0·705
	z	0·156	0·152	0·006	0·148
C_5	x	0·415	0·402	0·006	0·412
	y	0·767	0·682	0·030	0·770
	z	0·234	0·233	0·006	0·218
C_6	x	0·458	0·439	0·006	0·436
	y	0·580	0·577	0·030	0·640
	z	0·310	0·312	0·006	0·292
C_1'	x	0·610	0·619	0·006	0·617
	y	0·071	0·077	0·030	0·081
	z	0·312	0·308	0·006	0·307
C_2'	x	0·570	0·571	0·006	0·575
	y	0·130	0·121	0·030	0·150
	z	0·225	0·215	0·006	0·225
C_3'	x	0·570	0·576	0·006	0·572
	y	0·005	0·019	0·030	0·023
	z	0·145	0·142	0·006	0·150
C_4'	x	0·625	0·613	0·006	0·613
	y	0·821	0·824	0·030	0·827
	z	0·160	0·157	0·006	0·157
C_5'	x	0·665	0·665	0·006	0·656
	y	0·740	0·742	0·030	0·757
	z	0·248	0·243	0·006	0·239
C_6'	x	0·660	0·666	0·006	0·658
	y	0·870	0·846	0·030	0·883
	z	0·335	0·330	0·006	0·314
R	$h0l$	0·212	0·084	—	—
	$hk0$	0·261	0·155	—	—

Table 10. *Comparison of observed and calculated structure factors in p,p′-dichlorodiphenyl ditelluride, observed reflections only*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
00 00 02	131	120	06 00 10	31	30	15 00 07	20	11-
00 00 04	163	156-	06 00 12	31	32-	15 00 01-	51	48
00 00 06	307	287-	06 00 14	52	53-	15 00 03-	38	29
00 00 08	198	187-	06 00 16	23	26-	15 00 07-	40	47-
00 00 10	35	33	06 00 02-	80	76	15 00 09-	21	20-
00 00 12	124	121	06 00 04-	194	193	15 00 13-	23	33
00 00 14	66	69	06 00 06-	111	107	16 00 00	39	41
00 00 18	37	39-	06 00 08-	76	73-	16 00 04	30	32-
01 00 01	186	211	06 00 10-	152	138-	16 00 06	20	29-
01 00 03	31	32	06 00 12-	51	44-	16 00 02-	49	47
01 00 05	166	157-	06 00 16-	54	52	16 00 06-	37	40-
01 00 07	174	173-	06 00 18-	27	37	16 00 08-	40	40-
01 00 09	25	33-	07 00 01	106	103-	16 00 12-	18	22
01 00 11	97	102	07 00 03	144	145-	17 00 01	19	19
01 00 13	58	60	07 00 05	34	37-	17 00 01-	28	28
01 00 03-	41	41-	07 00 07	24	26	17 00 07-	24	29-
01 00 05-	228	191-	07 00 09	48	49			
01 00 07-	170	154-	07 00 11	36	25			
01 00 09-	35	37	07 00 15	23	17-			
01 00 11-	150	152	07 00 01-	47	43			
01 00 13-	44	46	07 00 03-	185	165	00 02 00	320	324-
01 00 17-	44	48-	07 00 05-	139	128	00 04 00	175	172
01 00 19-	28	39-	07 00 09-	85	84-	00 06 00	81	81-
02 00 00	98	103	07 00 11-	101	102-	00 08 00	24	37
02 00 02	55	60	07 00 13-	32	31-	01 02 00	21	5-
02 00 04	16	14-	07 00 15-	39	41	01 03 00	32	17-
02 00 06	56	57-	07 00 17-	28	31	01 04 00	52	51
02 00 08	31	36-	08 00 02	38	30	01 06 00	40	33-
02 00 02-	29	19	08 00 02-	51	36-	01 08 00	21	15
02 00 04-	96	86-	08 00 08-	32	16-	02 00 00	71	103
02 00 06-	123	112-	09 00 01	73	70	02 01 00	24	28-
02 00 08-	35	33-	09 00 03	90	93	02 02 00	85	86-
02 00 10	70	65	09 00 05	52	57	02 04 00	73	61
02 00 12-	70	71	09 00 07	36	38-	02 06 00	42	31-
02 00 18-	25	31-	09 00 09	66	64-	03 02 00	22	27-
03 00 01	44	43	09 00 11	23	23-	03 03 00	21	36
03 00 03	36	36	09 00 01-	58	62-	03 04 00	75	70
03 00 05	30	38	09 00 03-	107	105-	03 05 00	55	54-
03 00 07	45	48	09 00 05-	51	50-	03 06 00	48	44-
03 00 11	62	61-	09 00 07-	28	25	03 07 00	28	25
03 00 01-	16	5	09 00 09-	77	74	03 08 00	21	32
03 00 03-	44	37-	09 00 11-	25	21	04 00 00	286	315-
03 00 07-	27	30-	09 00 13-	25	24-	04 01 00	107	136
03 00 09-	41	39-	10 00 02	95	100	04 02 00	165	156
03 00 13-	36	34	10 00 04	89	92	04 03 00	97	96-
04 00 00	318	315-	10 00 08	75	78-	04 04 00	71	87-
04 00 02	233	284-	10 00 10	52	55-	04 05 00	58	51
04 00 04	40	34-	10 00 02-	97	106-	04 06 00	35	40
04 00 06	95	103	10 00 04-	87	93-	05 03 00	59	55
04 00 08	144	142	10 00 06-	33	13	05 05 00	32	26-
04 00 10	39	37	10 00 08-	90	85	06 00 00	137	121-
04 00 12	45	49-	10 00 10-	55	53	06 01 00	121	146
04 00 14	55	53-	10 00 12-	36	24-	06 02 00	92	92
04 00 02-	226	182	10 00 14-	23	34-	06 03 00	116	120-
04 00 04-	212	182	10 00 16-	27	31-	06 04 00	67	76-
04 00 06-	222	175	11 00 03	115	101	06 05 00	86	83
04 00 08-	41	41	11 00 05	69	68	06 06 00	44	43
04 00 10-	97	93-	11 00 09	54	49-	07 03 00	41	47-
04 00 12-	99	92-	11 00 11	37	33-	07 04 00	28	18-
04 00 16-	29	27	11 00 01-	101	95-	07 05 00	47	44
05 00 01	251	286-	11 00 03-	131	130-	09 01 00	33	31
05 00 03	164	177-	11 00 05-	39	37-	09 02 00	28	27-
05 00 05	18	27	11 00 07-	67	72	09 03 00	43	38-
05 00 07	165	177	11 00 09-	94	104	09 05 00	36	36
05 00 09	136	128	11 00 11-	44	47	10 01 00	162	126-
05 00 13	69	70-	11 00 13-	34	39-	10 03 00	112	97
05 00 15	47	47-	11 00 15-	43	52-	10 05 00	67	72-
05 00 01-	60	62-	12 00 04	66	63	12 00 00	46	17-
05 00 03-	206	192	12 00 06	30	27	12 01 00	97	68-
05 00 05-	246	214	12 00 10	29	29-	12 02 00	31	32
05 00 07-	68	69	12 00 02-	79	83-	12 03 00	73	57
05 00 09-	136	130-	12 00 04-	48	51-	12 05 00	37	28-
05 00 11-	136	123-	12 00 08-	66	70	14 01 00	39	27
05 00 15-	18	32	12 00 10-	31	27	14 02 00	27	20-
05 00 17-	52	51	12 00 14-	33	33-	14 04 00	27	29
06 00 00	112	121-	12 00 16-	18	22-	14 05 00	18	8
06 00 02	165	181-	14 00 04	33	31-	16 00 00	73	41
06 00 04	61	59-	15 00 01	23	19	16 01 00	57	17
06 00 06	79	77	15 00 03	30	21-	16 02 00	53	36-
06 00 08	130	130	15 00 05	35	37-	16 03 00	34	16-

The packing distances and bond angles in p,p′-dichlorodiphenyl diselenide are all reasonable. Although the dihedral angle of 74·5° along the Se–Se bond is smaller than the values usually found in similar situations, it is comparable to the values of 74·1° and 77·2° found in the $S_4^=$ ion (Abrahams, 1954). The corresponding dihedral angle in diphenyl diselenide was found to be 82° (Marsh, 1952).

The structure of *p,p′*-dichlorodiphenyl ditelluride

The structure of the ditelluride was refined by means of two-dimensional Fourier syntheses and least-squares cycles. The heavy-atom parameters in the diselenide were used to assign phases to the $h0l$ and $hk0$ structure factors at the start of the refinement. The usual procedures were followed in the Fourier refinement by use of F_o and F_c syntheses on (010) and on (001). The least-squares refinement of the x and z parameters by use of the $h0l$ data was also standard. However, owing to the availability of only 60 observed $hk0$ reflections, the $F(hk0)$ and $F(h0l)$ data were combined in the final least-squares cycles. Although the result was better than an independent refinement of the $hk0$ data, the standard deviations of the y parameters, especially of the carbon atoms, are quite large. These, in turn, lead to large standard deviations in the interatomic distances except for the Te–Te separation, the direction of which is almost parallel to (010). The atomic parameters and R values at two stages of the refinement are listed in Table 9. For comparison, a set of idealized carbon parameters are also given in the table. These were derived in the same manner as those for the diselenide. Observed and calculated structure factors for the $h0l$ and $hk0$ zones are compared in Table 10.

The bond distances, packing distances and bond angles based on the final least-squares parameters are given in Table 11. The observed Te–Te bonded separation of 2·702±0·010 Å appears to be significantly shorter than the value 2·74 Å computed from the accepted covalent single-bond radius (1·37 Å) for tellurium. Although this might be taken to indicate some double-bond character in this bond, a definite statement in this regard should await more information on the tellurium radius. The average of the observed Te–C bond distances, 2·13 Å, has been assigned a rather large standard deviation of 0·14 Å. While this value compares favorably with the radius sum, 2·14 Å, the uncertainties, both in the observed value and in the tellurium radius, make this comparison of little significance. A Te–C distance of 2·05±0·05 Å has been reported in di-*p*-tolyl telluride (Blackmore & Abrahams, 1955*b*), and unpublished work on diphenyl-tellurium dibromide, based on incompletely refined three-dimensional Fourier syntheses, indicates a Te–C distance of 2·12±0·03 Å (Christofferson & McCullough, 1956). As might be expected, the bond angles Te–Te′–C_1' and Te′–Te–C_1, which average 94·4°, are smaller than the corresponding angles in the diselenide, which average 101°. The dihedral angle of 72·0° in the ditelluride is slightly (but not significantly) smaller than the value 74·5° found in the diselenide.

Table 11. *Interatomic distances and bond angles in p,p′-dichlorodiphenyl ditelluride*

In same molecule		Between molecules		
Te–Te′	2·702 ± 0·010 Å	Te–Te′	4·18 Å	4·40* Å
Te–C_1	2·16 ± 0·20	Te–Te	4·43	4·40
Te′–C_1'	2·10 ± 0·20	Te–Cl	3·74	4·00
Te–C (ave.)	2·13 ± 0·14	Te′–Cl′	3·87	4·00
Cl–C_4	1·92 ± 0·22	Cl–Cl′	3·79	3·60
Cl′–C_4'	1·67 ± 0·22	C_2–C_5	3·64	3·70
Cl–C (ave.)	1·80 ± 0·16			
Te–Cl	6·69 ± 0·11	Angles		
Te′–Cl′	6·57 ± 0·11	Te–Te′–Cl′	95·2 ± 1·0°	
Te–Cl (ave.)	6·63 ± 0·08	Te′–Te–Cl	93·5 ± 1·0	
		Dihedral angle	72·0 ± 1·5	

* Sum of van der Waals radii.

Suggested mechanism for the twinning

As mentioned earlier, twinning on (001) is common in the diselenide and is the rule in the ditelluride. In the latter compound, most crystals exhibit a fine lamellar twinning on (001). A suggested explanation of the twinning is as follows: Consider the mid-point of the Se–Se (or Te–Te) bond in the central molecule in the upper half of Fig. 1. Pass a line through this point perpendicular to (001). Rotate the upper part of the figure (and the upper half of the crystal it now represents) through 180° about this axis. The result is a twinned crystal. The heavy atoms as well as carbon atoms C_1, C_4, C_1' and C_4' end up in positions at, or near, the former positions of like atoms. The van der Waals packing across the twin plane is almost identical to the packing across the (001) or (002) planes in the untwinned crystal. It is significant that on the projection of the structure on (010), the line joining Se′ and Cl′ is nearly parallel to the c axis in the original crystal, while the line joining Se and Cl is nearly parallel to the c axis of the twin.

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The Structure of $NiWO_4$

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The structure of $NiWO_4$ has been determined, using the Fourier difference method to locate the oxygen atoms. The structure is based on a distorted hexagonal close packing of oxygen atoms with Ni and W atoms each occupying one-fourth of the octahedral interstices. The Ni and W atoms lie off the centers of their respective octahedra by 0·13 Å and 0·30 Å.

1. Introduction

$NiWO_4$ is a member of the isomorphous series of tungstates of small cations which also includes $MgWO_4$, $MnWO_4$, $FeWO_4$, $CoWO_4$ and $ZnWO_4$. The structure of $MgWO_4$, with the exception of oxygen positions, was determined by Broch (1929). The unit cell is monoclinic (space group $P2/c$; $a = 4{\cdot}68$, $b = 5{\cdot}66$, $c = 4{\cdot}92$ Å, $\beta = 89°\,40'$) and contains two formula units. Atomic coordinates are:

2 Mg in (*e*): $\pm(\frac{1}{2}, y_{Mg}, \frac{1}{4})$,
2 W in (*f*): $\pm(0, y_W, \frac{1}{4})$,
4 O_I in (*g*): $\pm(x_1, y_1, z_1;\ x_1, \bar{y}_1, z_1+\frac{1}{2})$,
4 O_{II} in (*g*): $\pm(x_2, y_2, z_2;\ x_2, \bar{y}_2, z_2+\frac{1}{2})$,

with $y_{Mg} = 0{\cdot}68$ and $y_W = 0{\cdot}18$. It is suggested in *Strukturbericht* (1928–32) that the oxygen parameters are: $x_1 = 0{\cdot}20$, $y_1 = -0{\cdot}04$, $z_1 = 0{\cdot}10$, $x_2 = 0{\cdot}20$, $y_2 = 0{\cdot}40$, and $z_2 = 0{\cdot}40$. The structure as proposed in *Strukturbericht* is shown in Fig. 1.

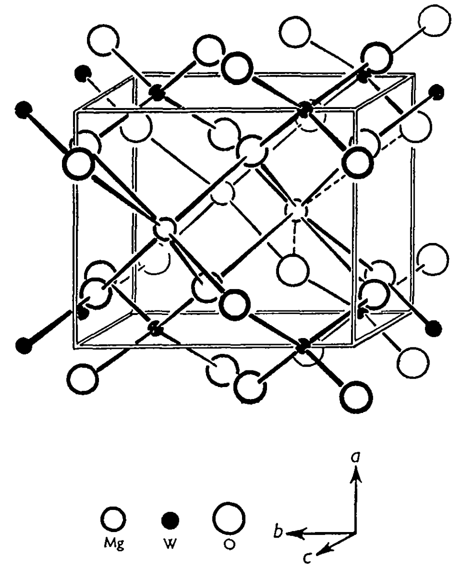

Fig. 1. The structure of $MgWO_4$ as proposed in *Strukturbericht*.

There are two objections to this structure. First, six of the eight oxygens surrounding Mg are assigned to a highly distorted MgO_6 octahedron. The remaining two oxygens, shown by broken lines in Fig. 1, are not considered a part of the coordination group although they lie just as close to Mg (2·27 Å and 3·01 Å) as do two of those in the octahedron. Second, the proposed oxygen parameters appear to be based largely on the assumption that W is surrounded by an oxygen tetrahedron. Since octahedral coordination is known to exist, as in WO_3 for example, this assumption is questionable.

With Broch's results on $MgWO_4$ as a starting point, the Fourier difference technique has been applied to the location of the oxygens in $NiWO_4$. The resulting oxygen positions give a structure which is not subject to the first of the aforementioned objections, and which contains WO_6 instead of WO_4 groups.

2. Experimental

Single crystals of $NiWO_4$ were grown from a melt of Na_2WO_4, $NiCl_2$, and NaCl in the ratio 1:2:2 by weight. This mixture was held at 900° C. for 2 hr. and then cooled slowly. Small dark brown, acicular crystals of $NiWO_4$, with the needle axis along *c*, were washed from the solidified melt with water.

Cell dimensions, as measured from a combination of powder and back-reflection single-crystal photographs, using Ni-filtered Cu $K\alpha$ radiation, are: