ACTA CHEMICA SCANDINAVICA 23 (1969) 1389–1397

The Crystal Structure of Tellurium Bis(diethylthioselenophosphinate)

STEINAR HUSEBYE

Chemical Institute, University of Bergen, Bergen, Norway

The crystal structure of tellurium bis(diethylthioselenophosphinate) has been determined and refined by three-dimensional X-ray methods. The structure consists of $(C_2H_5)_2P(S)-Se-Te-Se-P(S)(C_2H_5)_2$ molecules. The molecules have twofold symmetry with the tellurium atoms on twofold symmetry axes. One of the most interesting results of the analysis is the value found for the Te–Se bond length, 2.50 Å. Other bond lengths and angles are: Se–P = 2.26 Å, P=S = 1.93 Å, ∠Se–Te–Se′ = 100.7°, ∠Te–Se–P = 104.7°, and ∠Se–P–S = 103.8°. The dihedral angle Se′TeSe/TeSeP is 93.1°.

There are weak intermolecular Te···S bonds of length 3.65 Å joining the molecules together in a two-dimensional network. Each tellurium atom participates in two such bonds at a S···Te···S angle of 78.1°. These two bonds are roughly *trans* to the two Te–Se bonds of the molecule and a weak tendency to a square-planar coordination around the tellurium atom is thus found.

This structure work represents a continuation of the study of complex formation of divalent tellurium and selenium with bidentate dithio and related anionic ligands.[1–5] It was also felt that determination of the Te–Se bond length would be useful, as there at present is no such determination available.

The analogous compound, tellurium bis(dimethyldithiophosphate) [3] showed a distorted square-planar TeS_4 configuration where two sulfur atoms belong to the molecule proper and the other two belong to two neighbour molecules. Therefore a related structure was expected for tellurium bis(diethylthioselenophosphinate). Another structure described previously in this study, is that of tellurium di(ethylxanthate).[5] It also revealed a distorted square-planar configuration around the tellurium atom, but there the planar TeS_4 group consists of atoms belonging to one molecule only.

CRYSTAL DATA

The preparation of tellurium bis(diethylthioselenophosphinate) as well as unit cell, space group and IR data have been published recently.[4] The unit cell dimensions have been redetermined using sodium chloride calibrated Weissenberg photographs. The angle 2θ was then measured for 58 high order reflections. Using a least squares program "Celldim" made available by the Weizmann Institute, Rehovoth, Israel, and modified for use on the IBM 360—50H computer by Dr. Dove Rabinovich, the cell constants were then determined from the 2θ values mentioned above. The crystals are orange with $a=13.088\pm0.003$ Å, $b=12.379\pm0.002$ Å, $c=13.373\pm0.003$ Å, and $\beta=126.55\pm0.02°$. There are four molecules in the unit cell. Systematic absences, hkl for $h+k=2n+1$, $h0l$ for $l=2n+1$ and $0k0$ for $k=2n+1$, indicate either C_{2h}^6-C2/c or C_s^4-Cc as probable space groups. From analogy with the structure of tellurium bis(dimethyldithiophosphate)[3] where the tellurium atom lies on a twofold symmetry axis, the space group was assumed to be $C2/c$, as this space group possesses twofold symmetry axes and Cc does not. That the choice of space group was correct, was confirmed by the successful structure determination.

Intensity data for the $hk0$, $h0l$, $h1l$, $h2l$, $h3l$, and $h4l$ layers were estimated visually from integrated equi-inclination Weissenberg multiple-film photographs. Cu$K\alpha$ radiation was used for all layers. The crystals used for the b and c axis photographs had cross-sections of 0.09×0.08 and 0.08×0.06 mm^2, respectively. 674 out of 835 accessible reflections with $\sin\theta\leq0.985$ were observed and measured. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied.

STRUCTURE ANALYSIS

Coordinates for the tellurium and selenium atoms were found from Patterson maps, and the positions of the other atoms were found during subsequent Fourier refinements of the a and b axis projections. Because of overlap of sulphur and carbon peaks in the two projections the C_2 and C_4 carbon positions were uncertain.

The recorded three-dimensional data were then brought to a common scale, by comparison of reflections common to two layers. All unobserved reflections were removed from the data, likewise the strong reflections 110 and $\bar{1}11$ with $\sin\theta\leq0.1$, as the monitored program did not calculate reflections with so low values of $\sin\theta$. The reflection $\bar{1}31$ was caught by the camera screen and could therefore not be included in the data.

Structure refinement by least squares methods was then carried out on an IBM 1620[II] computer, using a block-diagonal program prepared by Mair.[6] Weighting scheme No. 3, recommended by Mair, was used with the constants a and b fixed at 29.8 and 18.6, respectively.

Following cycle two, anisotropic temperature factors were applied to the four heavy atoms. The correct position for C_4 was then found, and after the fourth cycle the scale factors for the different layers of reflections were adjusted by comparison of observed and calculated structure factors. An attempted

Table 1. Observed and calculated *hk*0, *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l* and *h*4*l* structure factors (×5) for tellurium bis(diethylthioselenophosphinate). Negative F_o values indicate unobserved reflections.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
0	2	0	223	187	2	0	4	713	736	3	1	9	-45	-10	-9	1	9	70	-70	8	2	1	184	166
0	4	0	136	143	2	0	6	276	-289	3	1	10	91	89	-9	1	10	194	191	8	2	2	216	219
0	6	0	685	-625	2	0	8	56	-39	3	1	11	-33	12	-9	1	11	52	51	8	2	3	196	-181
0	8	0	141	-111	2	0	10	97	88	5	1	1	149	-152	-9	1	12	115	-125	8	2	4	99	-105
0	10	0	65	53	2	0	12	-36	33	5	1	2	77	70	-9	1	13	122	-111	8	2	5	56	44
0	12	0	-38	-8	4	0	2	179	-174	5	1	3	230	212	-9	1	14	49	-44	8	2	6	-39	23
0	14	0	-37	7	4	0	4	387	358	5	1	4	267	262	-9	1	15	167	150	8	2	7	-25	66
1	1	0	316	246	4	0	6	242	-234	5	1	5	231	-238	-9	1	16	123	117	10	2	1	179	-161
1	3	0	364	-352	4	0	8	118	112	5	1	6	256	-281	-11	1	1	227	-235	10	2	2	94	89
1	5	0	251	-200	4	0	10	-42	-4	5	1	7	175	180	-11	1	2	212	-206	10	2	3	-43	-6
1	7	0	317	-284	6	0	2	168	-143	5	1	8	114	121	-11	1	3	207	203	10	2	4	91	-93
1	9	0	366	352	6	0	4	268	271	5	1	9	61	-44	-11	1	4	-43	-8	-2	2	1	-18	16
1	11	0	-38	43	6	0	6	226	-229	5	1	10	-23	37	-11	1	5	109	-114	-2	2	2	503	596
1	13	0	112	87	6	0	8	78	83	7	1	1	132	-132	-11	1	6	230	252	-2	2	3	260	-255
1	15	0	77	-70	8	0	2	122	112	7	1	2	214	202	-11	1	7	60	64	-2	2	4	602	-674
2	0	0	268	274	8	0	4	-52	-28	7	1	3	79	81	-11	1	8	256	-273	-2	2	5	29	30
2	2	0	879	-710	8	0	6	119	-118	7	1	4	133	-129	-11	1	9	123	-130	-2	2	6	317	365
2	4	0	128	112	10	0	2	103	-92	7	1	5	71	-86	-11	1	10	61	59	-2	2	7	107	93
2	6	0	207	-216	10	0	4	40	-46	7	1	6	-43	-1	-11	1	11	182	195	-2	2	8	189	-187
2	8	0	204	200	12	0	2	87	-107	7	1	7	97	92	-11	1	12	116	128	-2	2	9	216	-221
2	10	0	162	152	-2	0	2	210	167	7	1	8	-26	75	-11	1	13	226	-215	-2	2	10	157	158
2	12	0	-39	14	-2	0	4	434	-383	9	1	1	82	-79	-11	1	14	138	-139	-2	2	11	169	171
2	14	0	-36	-1	-2	0	6	-33	-38	9	1	2	54	47	-11	1	15	138	128	-2	2	12	63	-74
3	1	0	474	411	-2	0	8	221	228	9	1	3	45	45	-11	1	16	-34	15	-2	2	13	50	-61
3	3	0	56	11	-2	0	10	218	-236	9	1	4	67	-47	-13	1	1	82	-83	-2	2	14	-37	43
3	5	0	332	303	-2	0	12	187	194	9	1	5	48	-31	-13	1	2	95	92	-4	2	1	103	96
3	7	0	296	-300	-2	0	14	55	-47	9	1	6	-23	11	-13	1	3	43	42	-4	2	2	475	499
3	9	0	43	14	-4	0	2	239	157	11	1	1	139	-136	-13	1	4	158	-146	-4	2	3	180	-147
3	11	0	194	-190	-4	0	4	243	214	11	1	2	41	-34	-13	1	5	67	-57	-4	2	4	378	-409
3	13	0	63	38	-4	0	6	329	-347	11	1	3	-31	30	-13	1	6	82	76	-4	2	5	95	58
3	15	0	-26	-8	-4	0	8	551	560	-1	1	1	407	-650	-13	1	7	130	132	-4	2	6	280	290
4	0	0	73	64	-4	0	10	541	-546	-1	1	2	398	-390	-13	1	8	88	80	-4	2	7	189	189
4	2	0	372	-339	-4	0	12	191	194	-1	1	3	473	516	-13	1	9	150	-165	-4	2	8	168	-151
4	4	0	366	385	-4	0	14	-48	-13	-1	1	4	145	-137	-13	1	10	129	-145	-4	2	9	266	-253
4	6	0	48	-47	-6	0	2	233	-212	-1	1	5	96	-89	-13	1	11	165	178	-4	2	10	-44	0
4	8	0	-36	28	-6	0	4	580	559	-1	1	6	129	136	-13	1	12	108	124	-4	2	11	148	150
4	10	0	80	-79	-6	0	6	873	-924	-1	1	7	40	32	-13	1	13	102	-115	-4	2	12	-47	-20
4	12	0	-39	-31	-6	0	8	738	730	-1	1	8	112	-121	-13	1	14	48	-38	-4	2	13	-49	35
4	14	0	72	89	-6	0	10	112	-115	-1	1	9	137	-136	-13	1	15	46	42	-4	2	14	-45	33
5	1	0	429	-397	-6	0	12	150	-155	-1	1	10	148	-153	-13	1	16	-28	3	-4	2	15	96	-88
5	3	0	186	-185	-6	0	14	157	145	-1	1	11	147	152	-15	1	3	-20	34	-6	2	1	427	346
5	5	0	487	490	-6	0	16	43	35	-1	1	12	172	173	-15	1	4	-29	11	-6	2	2	345	335
5	7	0	-35	-8	-8	0	2	519	-489	-1	1	13	117	-113	-15	1	5	65	-70	-6	2	3	69	-53
5	9	0	117	123	-8	0	4	599	652	-1	1	14	89	-96	-15	1	6	54	-59	-6	2	4	198	-186
5	11	0	135	-144	-8	0	6	371	-372	-3	1	1	381	-357	-15	1	7	105	97	-6	2	5	300	-316
5	13	0	50	45	-8	0	8	127	-109	-3	1	2	271	238	-15	1	8	64	68	-6	2	6	50	23
6	0	0	87	-52	-8	0	10	198	213	-3	1	3	95	-12	-15	1	9	129	-136	-6	2	7	435	429
6	2	0	317	-304	-8	0	12	60	-48	-3	1	4	271	-258	-15	1	10	98	-107	-6	2	8	-38	-31
6	4	0	401	406	-8	0	14	166	-167	-3	1	5	133	-123	-15	1	11	126	128	-6	2	9	229	-232
6	6	0	91	110	-8	0	16	137	142	-3	1	6	87	78	-15	1	12	48	62	-6	2	10	210	195
6	8	0	-38	-12	-10	0	2	283	-274	-3	1	7	371	357	-15	1	13	66	-82	-6	2	11	128	-117
6	10	0	133	-149	-10	0	4	189	190	-3	1	8	398	387	-15	1	14	-31	1	-6	2	12	211	-209
6	12	0	79	-98	-10	0	6	63	-56	-3	1	9	364	-367	0	2	1	511	-679	-6	2	13	158	147
6	14	0	-22	38	-10	0	8	-48	39	-3	1	10	243	-244	0	2	2	181	185	-6	2	14	205	184
7	1	0	143	-131	-10	0	10	127	-136	-3	1	11	216	221	0	2	3	75	60	-6	2	15	-42	-31
7	3	0	-34	-28	-10	0	12	219	240	-3	1	12	49	51	0	2	4	258	-268	-6	2	16	57	-50
7	5	0	253	294	-10	0	14	194	-198	-3	1	13	70	-67	0	2	5	340	357	-8	2	1	183	-174
7	7	0	72	-92	-10	0	16	147	150	-3	1	14	106	93	0	2	6	403	429	-8	2	2	122	113
7	9	0	-40	27	-12	0	2	209	-215	-5	1	1	99	-107	0	2	7	224	-228	-8	2	3	439	424
7	11	0	136	-151	-12	0	4	160	168	-5	1	2	356	314	0	2	8	235	-236	-8	2	4	136	-124
7	13	0	57	64	-12	0	6	75	-81	-5	1	3	379	338	0	2	9	-46	9	-8	2	5	470	-452
8	0	0	121	128	-12	0	8	66	60	-5	1	4	41	-32	0	2	10	-46	52	-8	2	6	313	296
8	2	0	198	-214	-12	0	10	146	-171	-5	1	5	612	-555	0	2	11	136	143	-8	2	7	167	152
8	4	0	171	188	-12	0	12	220	248	-5	1	6	395	-352	0	2	12	-45	-29	-8	2	8	436	-442
8	6	0	-38	14	-12	0	14	214	-214	-5	1	7	523	535	0	2	13	121	-125	-8	2	9	168	165
8	8	0	-39	46	-12	0	16	71	79	-5	1	8	75	83	0	2	14	-21	23	-8	2	10	325	318
8	10	0	-38	-7	-14	0	2	-37	-31	-5	1	9	311	-278	2	2	1	531	-569	-8	2	11	108	-121
8	12	0	31	-35	-14	0	4	52	-54	-5	1	10	55	35	2	2	2	169	166	-8	2	12	202	-195
9	1	0	-38	26	-14	0	6	-50	36	-5	1	11	121	108	2	2	3	487	503	-8	2	13	-47	-18
9	3	0	80	-105	-14	0	8	158	148	-5	1	12	121	-118	2	2	4	53	-56	-8	2	14	47	41
9	5	0	-38	33	-14	0	10	259	-265	-5	1	13	65	-34	2	2	5	197	-207	-8	2	15	105	103
9	7	0	73	-90	-14	0	12	159	177	-5	1	14	61	61	2	2	6	50	51	-8	2	16	-36	-15
9	9	0	103	115	-14	0	14	-44	-26	-5	1	15	-38	8	2	2	7	122	-126	-10	2	1	242	-230
9	11	0	36	-37	-16	0	8	188	194	-7	1	1	249	-251	2	2	8	152	-164	-10	2	2	191	177
10	0	0	204	261	-16	0	10	98	-109	-7	1	2	-33	-9	2	2	9	189	188	-10	2	3	219	205
10	2	0	62	-90	-16	0	12	-35	37	-7	1	3	409	396	2	2	10	125	125	-10	2	4	289	-266
10	4	0	-39	1	1	1	1	508	-633	-7	1	4	225	222	2	2	11	77	-77	-10	2	5	-44	-20
10	6	0	118	-148	1	1	2	35	22	-7	1	5	495	-464	2	2	12	-31	-32	-10	2	6	276	290
10	8	0	-36	25	1	1	3	488	511	-7	1	6	196	-165	2	2	13	-27	-30	-10	2	7	127	-131
10	10	0	-26	48	1	1	4	43	-22	-7	1	7	294	275	4	2	1	75	-62	-10	2	8	157	-154
11	1	0	147	190	1	1	5	288	-290	-7	1	8	184	179	4	2	2	428	458	-10	2	9	117	112
11	3	0	-40	-36	1	1	6	231	221	-7	1	9	180	-170	4	2	3	334	336	-10	2	10	127	116
11	5	0	-38	-26	1	1	7	90	98	-7	1	10	-60	-38	4	2	4	283	-264	-10	2	11	-46	-20
11	7	0	81	-109	1	1	8	103	-107	-7	1	11	61	71	4	2	5	286	-263	-10	2	12	73	-69
12	0	0	91	149	1	1	9	-43	-46	-7	1	12	43	-22	4	2	6	138	138	-10	2	13	90	-81
12	2	0	51	-71	1	1	10	58	69	-7	1	13	-45	-14	4	2	7	139	137	-10	2	14	58	55
12	4	0	-35	-14	1	1	11	69	67	-7	1	14	-44	30	4	2	8	59	-49	-10	2	15	66	72
12	6	0	56	-102	1	1	12	-38	20	-7	1	15	-41	39	4	2	9	-45	-9	-10	2	16	-37	-21
13	1	0	-27	27	1	1	13	-24	-54	-7	1	16	-33	11	4	2	10	59	51	-12	2	1	90	-79
13	3	0	-24	-62	3	1	1	432	-438	-9	1	1	212	-207	6	2	1	217	209	-12	2	2	63	55
0	0	2	825	-1011	3	1	2	589	-617	-9	1	2	236	-244	6	2	2	124	107	-12	2	3	-48	11
0	0	4	204	197	3	1	3	407	437	-9	1	3	334	343	6	2	3	-44	9	-12	2	4	89	-81
0	0	6	217	213	3	1	4	314	329	-9	1	4	348	358	6	2	4	108	-86	-12	2	5	83	78
0	0	8	87	-74	3	1	5	305	-311	-9	1	5	289	-278	6	2	5	175	-175	-12	2	6	86	87
0	0	10	131	-156	3	1	6	52	-50	-9	1	6	267	-261	6	2	6	53	60	-12	2	7	136	-133
0	0	12	150	167	3	1	7	83	94	-9	1	7	195	187	6	2	7	124	120	-12	2	8	152	-162
2	0	2	983	-1175	3	1	8	146	-156	-9	1	8	-39	-41	6	2	8	74	-70	-12	2	9	-46	36

Table 1. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
-12	2	10	145	148	9	3	3	181	-169	-9	3	7	246	-226	2	4	5	-31	-27	-6	4	6	42	-15
-12	2	11	117	130	9	3	4	-38	-8	-9	3	8	-38	15	2	4	6	225	-220	-6	4	7	106	93
-12	2	12	76	-79	9	3	5	90	95	-9	3	9	429	454	2	4	7	212	-216	-6	4	8	114	114
-12	2	13	161	-164	9	3	6	-13	4	-9	3	10	70	59	2	4	8	198	201	-6	4	9	-33	-6
-12	2	14	-45	27	11	3	1	-39	-3	-9	3	11	333	-338	2	4	9	239	250	-6	4	10	187	-160
-12	2	15	123	117	11	3	2	-34	41	-9	3	12	77	-64	2	4	10	142	-139	-6	4	11	192	-164
-12	2	16	43	-45	-1	3	2	170	171	-9	3	13	86	83	2	4	11	94	-106	-6	4	12	200	199
-14	2	2	72	75	-1	3	3	326	-357	-9	3	14	93	84	4	4	1	81	90	-6	4	13	184	179
-14	2	3	60	-57	-1	3	4	-24	-48	-9	3	15	86	80	4	4	2	77	-56	-6	4	14	127	-107
-14	2	4	140	-135	-1	3	5	587	686	-9	3	16	40	-39	4	4	3	-31	-12	-6	4	15	65	-69
-14	2	5	100	87	-1	3	6	57	-58	-11	3	1	135	-95	4	4	4	-33	-36	-8	4	1	64	40
-14	2	6	188	181	-1	3	7	538	-581	-11	3	2	56	54	4	4	5	-35	-28	-8	4	2	106	-87
-14	2	7	-46	43	-1	3	8	93	-95	-11	3	3	-41	-2	4	4	6	-36	46	-8	4	3	210	185
-14	2	8	148	-128	-1	3	9	236	225	-11	3	4	-41	-41	4	4	7	55	49	-8	4	4	58	-29
-14	2	9	207	-196	-1	3	10	54	56	-11	3	5	235	223	4	4	8	75	74	-8	4	5	171	-163
-14	2	10	52	65	-1	3	11	-42	27	-11	3	6	104	102	4	4	9	-33	15	-8	4	6	101	-91
-14	2	11	178	194	-1	3	12	-41	-28	-11	3	7	373	-406	4	4	10	70	-82	-8	4	7	110	-99
-14	2	12	57	-69	-1	3	13	81	-81	-11	3	8	131	-137	6	4	1	292	263	-8	4	8	167	150
-14	2	13	77	-82	-1	3	14	-27	0	-11	3	9	212	222	6	4	2	335	-301	-8	4	9	231	235
-14	2	14	105	113	-3	3	1	631	736	-11	3	10	58	87	6	4	3	74	-75	-8	4	10	240	-252
-14	2	15	51	-54	-3	3	2	110	93	-11	3	11	-42	14	6	4	4	72	67	-8	4	11	139	-141
-16	2	7	88	123	-3	3	3	1024	-1217	-11	3	12	101	-94	6	4	5	-38	-26	-8	4	12	151	148
-16	2	8	47	-44	-3	3	4	64	45	-11	3	13	114	-111	6	4	6	-37	11	-8	4	13	-38	44
-16	2	9	88	-86	-3	3	5	672	740	-11	3	14	67	67	6	4	7	-34	12	-8	4	14	58	-48
-16	2	10	71	78	-3	3	6	165	138	-11	3	15	-37	30	6	4	8	28	-39	-8	4	15	44	32
-16	2	11	-32	-6	-3	3	7	145	-132	-11	3	16	62	-56	8	4	1	316	292	-8	4	16	-24	-18
-16	2	12	89	-94	-3	3	8	90	-87	-13	3	1	61	47	8	4	2	227	-217	-10	4	1	89	-75
1	3	1	291	-269	-3	3	9	204	-204	-13	3	2	60	64	8	4	3	236	-225	-10	4	2	-36	48
1	3	2	301	436	-3	3	10	99	88	-13	3	3	208	-176	8	4	4	176	167	-10	4	3	-36	-9
1	3	3	44	-32	-3	3	11	128	132	-13	3	4	44	-65	8	4	5	94	93	-10	4	4	77	66
1	3	4	303	-334	-3	3	12	79	-64	-13	3	5	234	237	8	4	6	48	-44	-10	4	5	197	185
1	3	5	227	232	-3	3	13	78	69	-13	3	6	42	56	10	4	1	70	-66	-10	4	6	190	-167
1	3	6	106	101	-3	3	14	61	51	-13	3	7	135	-126	10	4	2	87	-79	-10	4	7	187	-205
1	3	7	235	-242	-5	3	1	681	763	-13	3	8	42	-31	10	4	3	55	-38	-10	4	8	269	307
1	3	8	-40	26	-5	3	2	59	41	-13	3	9	-42	42	10	4	4	63	84	-10	4	9	147	152
1	3	9	189	199	-5	3	3	292	-287	-13	3	10	78	75	12	4	1	-25	33	-10	4	10	190	-198
1	3	10	55	45	-5	3	4	229	-211	-13	3	11	-42	-15	-2	4	1	271	280	-10	4	11	140	-154
1	3	11	90	-75	-5	3	5	127	-86	-13	3	12	61	-70	-2	4	2	348	-386	-10	4	12	84	87
1	3	12	-32	-40	-5	3	6	265	241	-13	3	13	93	77	-2	4	3	293	-312	-10	4	13	75	81
1	3	13	-15	4	-5	3	7	276	254	-13	3	14	58	47	-2	4	4	421	463	-10	4	14	-36	5
3	3	1	113	104	-5	3	8	285	-266	-13	3	15	93	-109	-2	4	5	169	168	-10	4	15	-32	-43
3	3	2	31	29	-5	3	9	45	-19	-13	3	16	-23	19	-2	4	6	326	-318	-10	4	16	-25	-5
3	3	3	175	160	-5	3	10	167	154	-15	3	4	-24	-1	-2	4	7	-37	8	-12	4	1	-34	39
3	3	4	142	-134	-5	3	11	196	-179	-15	3	5	104	108	-2	4	8	106	85	-12	4	2	78	-74
3	3	5	-37	7	-5	3	12	47	-65	-15	3	6	-33	20	-2	4	9	-35	-50	-12	4	3	114	-100
3	3	6	144	140	-5	3	13	168	186	-15	3	7	94	-89	-2	4	10	-36	53	-12	4	4	192	172
3	3	7	198	-212	-5	3	14	-40	-7	-15	3	8	77	-63	-2	4	11	-38	-12	-12	4	5	158	143
3	3	8	58	-71	-5	3	15	114	-105	-15	3	9	-37	36	-2	4	12	-37	-31	-12	4	6	274	-275
3	3	9	168	172	-7	3	1	177	157	-15	3	10	58	47	-2	4	13	-34	27	-12	4	7	199	-202
3	3	10	-38	-5	-7	3	2	203	191	-15	3	11	43	-31	-2	4	14	-25	-22	-12	4	8	186	180
3	3	11	71	-84	-7	3	3	68	-86	-15	3	12	-33	-24	-4	4	1	89	104	-12	4	9	200	205
5	3	1	549	594	-7	3	4	289	-270	-15	3	13	47	47	-4	4	2	490	-507	-12	4	10	83	-88
5	3	2	116	89	-7	3	5	62	-13	-15	3	14	-25	-19	-4	4	3	380	-347	-12	4	11	71	-58
5	3	3	168	-145	-7	3	6	267	253	0	4	1	53	41	-4	4	4	351	360	-12	4	12	-37	-2
5	3	4	-39	-38	-7	3	7	145	-137	0	4	2	172	-178	-4	4	5	316	329	-12	4	13	51	-49
5	3	5	91	-90	-7	3	8	56	-48	0	4	3	241	-244	-4	4	6	158	-156	-12	4	14	-34	-12
5	3	6	-42	26	-7	3	9	255	234	0	4	4	351	371	-4	4	7	165	-160	-12	4	15	51	64
5	3	7	71	75	-7	3	10	-39	-30	0	4	5	450	511	-4	4	8	-31	-25	-14	4	3	104	-99
5	3	8	-40	-18	-7	3	11	309	-314	0	4	6	347	-352	-4	4	9	45	67	-14	4	4	157	148
5	3	9	64	70	-7	3	12	-41	34	0	4	7	348	-347	-4	4	10	-36	-33	-14	4	5	145	139
7	3	1	285	282	-7	3	13	276	248	0	4	8	241	243	-4	4	11	-36	-8	-14	4	6	117	-92
7	3	2	96	92	-7	3	14	-42	-5	0	4	9	-36	47	-4	4	12	108	99	-14	4	7	79	-66
7	3	3	265	-254	-7	3	15	123	-105	0	4	10	52	-63	-4	4	13	71	53	-14	4	8	63	38
7	3	4	78	-77	-7	3	16	40	-45	0	4	11	73	79	-4	4	14	144	-127	-14	4	9	50	-68
7	3	5	98	80	-9	3	1	160	153	0	4	12	-33	-27	-4	4	15	87	-94	-14	4	10	-35	19
7	3	6	63	69	-9	3	2	149	120	0	4	13	36	-53	-6	4	1	564	576	-14	4	11	110	103
7	3	7	-34	19	-9	3	3	-38	-7	2	4	1	77	72	-6	4	2	333	-328	-14	4	12	-33	13
9	3	1	217	218	-9	3	4	108	-82	2	4	2	42	-38	-6	4	3	398	-417	-14	4	13	-31	-20
9	3	2	-43	7	-9	3	5	64	64	2	4	3	79	62	-6	4	4	207	193	-14	4	14	58	-60
					-9	3	6	52	-51	2	4	4	62	51	-6	4	5	77	58	-16	4	10	27	-26

introduction of anisotropic temperature factors for the carbon atoms proved fruitless, as the reliability index $R=\sum||F_o|-|F_c||/\sum|F_o|$ increased as did the standard deviations in atomic parameters. After the tenth cycle of least squares refinement the strong reflections 002, 111, and 021 which had consistently much higher calculated than observed values, were removed from the data as this effect was attributed to secondary extinction. The observed reflection $\bar{3}13$ which had a calculated value close to zero was also removed. This latter effect remains obscure. A final structure factor calculation based on the parameter output from the last (12th) refinement cycle was then carried out for all reflections with sin $\theta \leq 0.985$. The R-value for this material, with non-observed reflections included only when F_c exceeds the observable limit, is 0.087.

The final atomic coordinates and thermal parameters are listed in Tables 2 and 3. In Table 1 are listed the observed structure factors, and those calculated using the parameters in Tables 2 and 3. The calculated structure factors are based on atomic scattering factors for tellurium by Thomas and Umeda,[7] for selenium and phosphorus by Freeman and Watson,[8] for sulfur by Dawson,[9] and for carbon by Hoerni and Ibers.[10] The factors for tellurium and selenium were corrected for anomalous dispersion according to Cromer.[11] Interatomic distances and angles based on the parameters of Table 2, are listed in Tables 4 and 5.

Table 2. Atomic coordinates for tellurium bis(diethylthioselenophosphinate) in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z
Te	0.0000	0.2246	0.2500
Se	0.0875	0.0957	0.1745
S	0.3480	−0.0462	0.2853
P	0.2864	0.0587	0.3442
C_1	0.2796	0.0160	0.4714
C_2	0.2229	−0.0868	0.4558
C_3	0.3743	0.1842	0.3993
C_4	0.4173	0.2298	0.3257

Table 3. Temperature parameters $\beta_{ij} \times 10^{-3}$. The expression used is $\exp-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+kl\beta_{23}+hl\beta_{13}+hk\beta_{12})$.

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Te	7.60	7.41	10.08	0.00	11.97	0.00
Se	6.73	7.58	6.16	−0.25	7.71	1.12
S	9.45	8.15	10.66	−1.13	13.56	6.09
P	6.01	3.96	6.16	0.42	7.65	−0.46

For the carbon atoms, a temperature factor $\exp -B(\sin^2\theta/\lambda^2)$ is used with $B=3.42$, 4.76, 4.56, and 5.77 for C_1, C_2, C_3, and C_4, respectively.

Table 4. Bond lengths and angles in tellurium bis(diethylthioselenophosphinate).

Te−Se	2.501±0.003 Å	∠Se−Te−Se′	= 100.7±0.2°
Se−P	2.258±0.010	∠Te−Se−P	= 104.7±0.3
P−S	1.926±0.011	∠Se−P−S	= 103.8±0.6
P−C_1	1.83 ±0.03	∠Se−P−C_1	= 109.1±1.2
P−C_3	1.81 ±0.04	∠Se−P−C_3	= 108.0±1.6
C_1−C_2	1.42 ±0.05	∠S−P−C_1	= 116.6±1.2
C_3−C_4	1.50 ±0.04	∠S−P−C_3	= 115.2±1.0
		∠C_1−P−C_3	= 103.9±1.7
		∠P−C_1−C_2	= 115.5±2.5
		∠P−C_3−C_4	= 116.8±2.8

Table 5. Other interatomic distances and angles.

Te—P	= 3.77 Å	P—C_4	= 2.83 Å
Te—C_1	= 3.99	Se—Se′	= 3.85
Te—C_3	= 4.07	Te—S(I)	= 3.654 ± 0.005
Se—S	= 3.30		
Se—C_1	= 3.34	∠Se—Te—S(II)	= 91.6°
Se—C_2	= 3.80	∠Se—Te—S(I)	= 164.4
Se—C_3	= 3.30	∠S(I)—Te—S(II)	= 78.1
Se—C_4	= 3.88		
S—C_1	= 3.20		
S—C_2	= 3.55		
S—C_3	= 3.15		
S—C_4	= 3.49		
P—C_2	= 2.76		

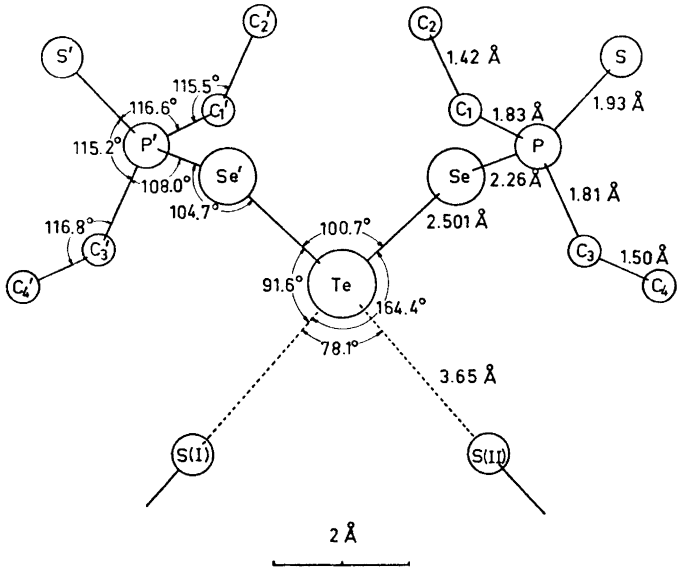

Fig. 1. The tellurium bis(diethylthioselenophosphinate) molecule and the configuration around the tellurium atom seen along the normal to the least squares plane through the $TeSe_2S_2$ group. I and II indicate atoms in molecules which are related to the original one by the screw axes (−1/4, *y*, 1/4) and (1/4, *y*, 1/4) respectively. Primed letters denote atoms in one half of the molecule related to the other half (Table 2) by a twofold symmetry axis through the tellurium atom.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION OF THE RESULTS

In Fig. 1 is shown the tellurium bis(diethylthioselenophosphinate) molecule and the approximate planar $TeSe_2S_2$ group with calculated bond lengths and angles. The packing of the molecules seen along the *c* axis is visualized in Fig. 2.

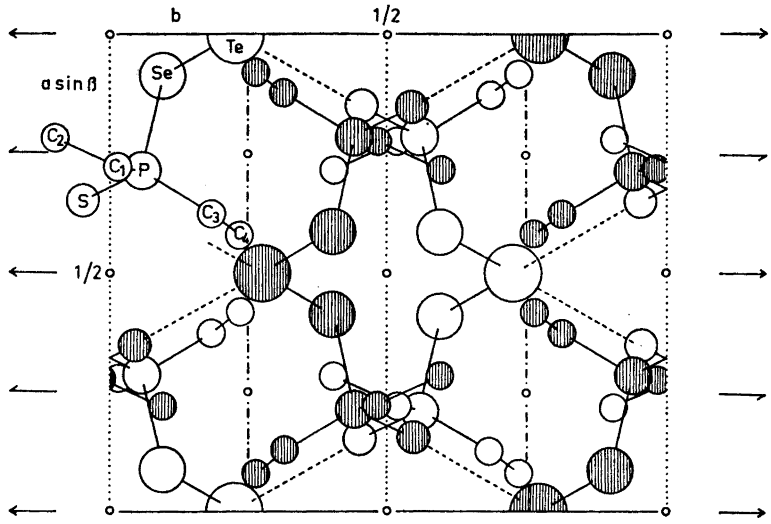

Fig. 2. The packing of the tellurium bis(diethylthioselenophosphinate) molecules seen along *c*. Filled circles represent atoms in molecules at *c*/2 above the others. In the upper left corner, one molecule is removed to show the atoms in the asymmetric unit more clearly.

The structure consists of tellurium bis(diethylthioselenophosphinate) molecules, with a twofold symmetry axis parallel to the *b*-axis, through each tellurium atom. A comparison with the analogous compound, tellurium bis(dimethyldithiophosphate),[3] reveals a marked resemblance in the shapes of the molecules and the arrangement around the central tellurium atom. However, in the present case, the tendency to square-planar coordination around the central tellurium atom is less pronounced.

The least squares plane through the $TeSe_2S_2$ group mentioned above, obeys the equation: $0.268\ X+0.963\ Z-2.056=0$. It is based on coordinates given in Ångströms, and refers to an orthogonal coordinate system obtained by putting the *c* axis normal to *a* and *b*. The plane passes through the tellurium atom while Se is 0.31 Å above and Se′ is 0.31 Å below the plane. The two sulphur atoms of the group, belonging to different neighbour molecules (Fig. 1) are 0.24 Å on each side of the plane, S(I) being above and S(II) below. Thus the planarity of the group is less pronounced than that of the analogous TeS_4 group in tellurium bis(dimethyldithiophosphate).[3]

The weak intermolecular Te···S bonds as exemplified by the Te···S(I) and Te···S(II) bonds in Fig. 1, have a length of 3.65 Å in the present case, as compared to 3.31 Å in the dithiophosphate [3] and 4.05 Å for the sum of the corresponding van der Waals radii.[12] Each tellurium atom participates in two such bonds, which link the molecules together in layers.

The angles at the central tellurium atom deviate significantly from 90° and 180° except for the Se—Te—S(II) and Se′—Te—S(I) angles which are

91.6°. The Se—Te—S angles in the $TeSe_2S_2$ group where the selenium and sulphur atoms are *trans* to each other are 164.4°. Thus from consideration of angles and bond lengths, the Te—Se and Te···S bonds are very unequal of length (Tables 4 and 5) as compared to respective covalent bonds and they make an angle which is about 165°. The sum of the lengths of the Te—Se and Te···S bonds is 6.15 Å — considerably longer than the value of 5.49 Å based on the Pauling covalent radii for sulphur and selenium and on the radius of 1.64 Å found for tellurium in some other square planar complexes of divalent tellurium.[13] This greater bonding radius for tellurium has been explained by assuming three-center four-electron bonding, using *p*-orbitals on tellurium and the two atoms bonded to it *trans* to each other.[13,14] In the present case, the extra long S···Te—Se length may probably be explained on basis of great asymmetry in bond strength. The limit of two such *trans* bonds would be a single covalent bond *trans* to a no-bond contact.[13] In the present case, the Te—Se bond length is close to the expected covalent bond length (see below). The S···Te weak bond is 3.65 Å as compared to 3.59 Å, the latter value being the sum of the no-bond radii of 1.68 and 1.91 Å tentatively proposed for sulphur and tellurium in this connection.[13]

Inspection of the molecule show that the P—Se—Te—Se—P chain again has the *trans* configuration.[3] Certain interplanar angles have been calculated, and the angles Se′TeSe/TeSeP, Se′TeSe/SePS, SePS/C_1PC_3, and the angle between the plane through SePS and the least squares plane through TeSePS, are found to be 93.1, 92.4, 90.1, and 1.9° respectively.

From Table 5, it is seen that the Te—Se bond length is 2.501±0.004 Å as compared to the sum of covalent radii corrected for polarity,[15] which is 2.52 Å. The observed P—Se bond length of 2.26 Å agrees well with the corresponding bond length of 2.28 Å found in bis(diethylthiophosphoryl) diselenide,[16] and the corrected sum of covalent radii which is 2.24 Å. As expected, the P=S double bond length of 1.93 Å is very close to the corresponding lengths of 1.92 and 1.93 Å found in tellurium bis(dimethyldithiophosphate)[3] and the diselenide,[16] respectively.

The P—C and C—C bond lengths are not significantly different from covalent single bond lengths.

The Se—Te—Se′ angle is 100.7°. This is a little larger than the S—Te—S′ angle in tellurium bis(dimethyldithiophosphate)[3] which is 98.3°. Also the Se′TeSe/TeSeP dihedral angle of 93.1° is not much different from the corresponding angle of 90.7° found in the dimethyldithiophosphate.[3] In so far as the Te—Se—P angle is concerned, the value of 104.7° found in the present study agrees well with the values of 106.2° found for the selenium valency angle in bis(diethylthiophosphoryl) diselenide[16] and the angles of 103.1—105.9° found in elementary selenium.[17-20]

On the phosphorus atom, the angles vary between 103.8 and 116.6°, the average is 109.4° which corresponds to tetrahedral hybridization. However, both in the present case and in the dithiophosphate[3] and diselenide[16] mentioned above, the two largest angles are $\angle S—P—C_1$ and $\angle S—P—C_3$ and the corresponding ones in the two other structures. In all the three cases cited, these two angles are between 115 and 117.5° while the other angles on phosphorus in the same compounds are below 109.1°. This effect may be due to

repulsion between the double-bonded sulfur atom and the alkyl/alkoxy substituents on phosphorus. The $P-C_1-C_2$ and $P-C_3-C_4$ angles are large, 116 and 117° respectively; however, in view of the large standard deviations in these angles, the deviation from the tetrahedral angle is not significant.

There are no especially short intermolecular contacts, except for the weak Te···S bond mentioned above.

REFERENCES

1. Husebye, S. *Acta Chem. Scand.* **19** (1965) 1045.
2. Husebye, S. *Acta Chem. Scand.* **19** (1965) 774.
3. Husebye, S. *Acta Chem. Scand.* **20** (1966) 24.
4. Husebye, S. *Acta Chem. Scand.* **20** (1966) 2007.
5. Husebye, S. *Acta Chem. Scand.* **21** (1967) 42.
6. Mair, G. A. *Structure Factor and Least Squares Programs for the IBM 1620*, National Research Council, Ottawa 1963.
7. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
8. Freeman, A. J. and Watson, R. E. *International Tables of Crystallography*, Kynoch Press, Birmingham 1962, Vol III, p. 202.
9. Dawson, B. *Acta Cryst.* **13** (1960) 403.
10. Hoerni, J. A. and Ibers, J. A. *Acta Cryst.* **7** (1954) 744.
11. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
12. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
13. Foss, O. *Acta Chem. Scand.* **16** (1962) 779.
14. Foss, O. and Husebye, S. *Acta Chem. Scand.* **20** (1966) 132.
15. Schomaker, V. and Stevenson, D. P. *J. Am. Chem. Soc.* **63** (1941) 37.
16. Husebye, S. *Acta Chem. Scand.* **20** (1966) 51.
17. Burbank, R. D. *Acta Cryst.* **4** (1951) 140.
18. Marsh, R. E., Pauling, L. and McCullough, J. D. *Acta Cryst.* **6** (1953) 71.
19. Cherin, P. and Unger, P. The 7th Int. Congress and Symposium in Crystallography, Moscow, July 12—21, 1966; *Acta Cryst.* **21 part 7** (1966), p. A 46.
20. Cherin, P. and Unger, P. *Inorg. Chem.* **6** (1967) 1589.

Received July 3, 1968.