The Crystal and Molecular Structure of Selenium Bis(diethyldiselenophosphinate)

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The crystal and molecular structure of the triselenide selenium bis(diethyldiselenophosphinate) $Se[Et_2PSe_2]_2$, has been solved and refined by three-dimensional X-ray methods. The refinement comprises the $hk0$, $h0l$, $h1l$, $h2l$, $h3l$, and $h4l$ reflections. Anisotropic temperature parameters were used for the heavy atoms.

The monoclinic crystals belong to the space group $C_{2h}^6 - C2/c$ with four formula units per unit cell. The molecules possess twofold symmetry axes passing through the central selenium atoms.

In the crystal, each central selenium atom in addition to being bonded to two selenium atoms in the molecule, forms close contacts with two selenium atoms from neighbour molecules.

The resulting four-coordinate $SeSe_4$ arrangement is nearly planar. The intermolecular $Se\cdots Se$ contacts of 3.68 Å give rise to a loose two-dimensional association of molecules.

Some relevant data are:
$Se_1-Se_2=2.35$ Å, $Se_2-P=2.24$ Å, $P-Se_3=2.10$ Å, $\angle Se_2'-Se_1-Se_2 = 103.9°$, $\angle Se_1-Se_2-P=105.0°$ and $\angle Se_2-P-Se_3=103.1°$. The dihedral angle, $Se_2'Se_1Se_2/Se_1Se_2P=92.5°$.

During our study of compounds of divalent tellurium and selenium with dithio- and related anions,[1-6] so far only crystal structures of tellurium compounds have been determined. The present work represents the first structure investigation of a divalent selenium compound in this connection.

The structure of selenium bis(diethyldiselenophosphinate) was expected to reveal the same tendency to square-planar coordination around the central selenium atom, as was found for the tellurium atom in tellurium bis(diethyl-thioselenophosphinate).[6] The work would also provide information about the structure of triselenides. Such data seem to be rather scarce.[7]

Selenium bis(diethyldiselenophosphinate), or bis(diethylselenophosphoryl) triselenide, $Et_2P(Se)-Se-Se-Se-P(Se)Et_2$, was first isolated by Kuchen and Knop.[8] The crystals are isomorphous with those of tellurium bis(diethyl-thioselenophosphinate),[4] the structure of which has recently been worked out in this laboratory,[6] and also with the crystals of selenium bis(diethyl-thioselenophosphinate).[4]

EXPERIMENTAL

Preparation of the crystals, and space group, IR and unit cell data have been reported earlier.[4] However, the unit cell parameters have been redetermined in connection with the present structure investigation. A least squares program, "Celldim", made available by the Weizmann Institute, Rehovoth, Israel and modified for use on an IBM 360−50H computer by Dr. Dove Rabinovich, was used in the calculation of cell constants. The calculation was based on values of the angle 2θ for 77 high order reflections measured from sodium chloride calibrated Weissenberg photographs. The orange crystals are prisms extended along the c-axis with $a = 12.906 \pm 0.003$ Å, $b = 12.450 \pm 0.003$ Å, $c = 13.412 \pm 0.003$ Å and $\beta = 124.84 \pm 0.02°$. There are four formula units per unit cell and the space group, from systematic extinctions and comparison with the isomorphous compound, tellurium bis(diethylthioselenophosphinate), is $C_{2h}^6 - C2/c$ (No. 15).

The intensities of the $hk0$, $h0l$, $h1l$, $h2l$, $h3l$, and $h4l$ reflections were estimated visually from sets of integrated equi-inclination Weissenberg photographs, taken with $CuK\alpha$ radiation. The cross sections of the crystal specimens used, were 0.09×0.09 mm² and 0.07×0.08 mm² for the b and c axis photographs, respectively. 721 independent reflections were observed and measured. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Common reflections in the six layers were used, to put all reflections on the same scale.

Least squares block-diagonal refinement was carried out on an IBM 1620 [II] computer, using a program designed by Mair.[9] Weighting scheme No. 3 in this program was used. During the final stages of refinement, factors a and b in this scheme, were put equal to 16 and 10 respectively.

STRUCTURE DETERMINATION

The structure determination was begun in a straightforward way by assigning trial positions to the atoms in the asymmetric unit in accord with the positions found for the corresponding atoms in the isomorphous tellurium bis(diethylthioselenophosphinate). The structure improved during subsequent Fourier refinements of the b and c axis projections. There is half a molecule in the asymmetric unit, with twofold symmetry axes parallel to b running through the central selenium atoms in the crystal.

The structure was further refined by means of least squares methods. The refinement included the $hk0$, $h0l$, $h1l$, $h2l$, $h3l$, and $h4l$ reflections, with common reflections removed from the recordings around the b axis. Likewise, unobserved reflections were not included in the refinement. In addition, the six reflections 020, 110, 002, 111, $\bar{1}11$, and 202 were not included in all refinement cycles because of temporary very poor agreement between the observed and calculated values. After allocation of anisotropic temperature factors to the heavy atoms, all reflections were rescaled relative to each other by comparison between the observed and calculated structure factors. Low order reflections which were assumed to be affected by secondary extinction were given zero weight in the final stages of refinement. They are indicated by asterisks in Table 1.

The final value of the reliability index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ is 0.079. This value is based on all reflections of Table 1, excluding only the unobserved reflections where F_c does not exceed the observable limit.

Final observed and calculated structure factors are listed in Table 1. Calculated values are based on atomic scattering factors for selenium and phosphorus by Freeman and Watson,[10] and for carbon by Hoerni and Ibers.[11]

Table 1. Observed and calculated hk0, h0l, h1l, h2l, h3l, and h4l structure factors (×5) for selenium bis(diethyldiselenophosphinate). Unobserved reflections are indicated by negative F_O values.

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)
C	2	0	488	593*	0	0	14	-10	-13	3	1	6	58	-59	-9	1	3	197	219	6	2	3	37	-36
0	4	0	72	73	2	0	2	1204	1073*	3	1	7	95	94	-9	1	4	400	398	6	2	4	101	-96
C	6	C	47C	-494	2	0	4	8C4	8C4	3	1	8	100	-109	-9	1	5	148	-145	6	2	5	100	-96
0	8	C	25C	-233	2	0	6	353	-401	3	1	9	-27	-22	-9	1	6	339	-377	6	2	6	79	72
C	10	C	57	61	2	0	8	52	65	3	1	10	78	80	-9	1	7	66	72	6	2	7	95	95
C	12	0	77	-83	2	0	10	47	58	3	1	11	-23	3	-9	1	8	101	102	6	2	8	55	-54
0	14	C	-26	-8	2	0	12	-15	0	3	1	12	-38	-47	-9	1	9	64	60	6	2	9	52	-57
1	1	0	41	36*	4	0	2	193	209	5	1	1	30	32	-9	1	10	71	69	8	2	1	164	155
1	3	C	432	-487	4	0	4	74	81	5	1	2	-26	-3	-9	1	11	83	-79	8	2	2	64	64
1	5	C	263	-254	4	0	6	133	-151	5	1	3	54	46	-9	1	12	66	-63	8	2	3	195	-193
1	7	C	168	-173	4	0	8	97	124	5	1	4	306	294	-9	1	13	-27	-14	8	2	4	-24	-19
1	9	C	313	332	4	0	10	27	-31	5	1	5	110	-114	-9	1	14	38	-39	8	2	5	85	81
1	11	0	115	127	6	0	2	-17	7	5	1	6	278	-296	-9	1	15	79	72	8	2	6	-21	-3
1	13	C	34	38	6	0	4	52	67	5	1	7	108	116	-9	1	16	75	69	8	2	7	-17	6
1	15	C	27	-21	6	0	6	50	-6C	5	1	8	152	149	-9	1	17	54	-58	10	2	1	173	-170
2	0	0	26	44	6	0	8	18	19	5	1	9	34	-32	-11	1	1	130	-128	10	2	2	31	28
2	2	C	490	-543	8	0	2	26	25	5	1	10	-18	-11	-11	1	2	213	-214	10	2	3	31	28
2	4	0	-15	-5	8	0	4	-19	-20	7	1	1	89	-89	-11	1	3	89	88	10	2	4	36	-39
2	6	C	48	-55	8	0	6	44	-81	7	1	2	245	256	-11	1	4	54	46	10	2	5	39	48
2	8	C	102	104	8	0	8	74	-83	7	1	3	-26	8	-11	1	5	-26	-21	12	2	1	65	-63
2	10	C	175	182	10	0	4	23	-P4	7	1	4	167	-174	-11	1	6	161	173	12	2	2	37	37
2	12	C	37	-27	12	0	2	38	-42	7	1	5	-27	-8	-11	1	7	-26	-15	-2	2	1	-9	-5
2	14	C	-26	3	-2	0	2	547	447	7	1	6	36	31	-11	1	8	197	-215	-2	2	2	518	510
3	1	C	475	549	-2	0	4	855	-682	7	1	7	43	36	-11	1	9	38	-36	-2	2	3	314	-107
3	3	C	168	158	-2	0	6	440	374	7	1	8	56	56	-11	1	10	98	101	-2	2	4	842	-675
3	5	C	306	3C5	-2	0	8	138	-149	9	1	1	54	-52	-11	1	11	104	109	-2	2	5	89	-80
3	7	C	300	-287	-2	0	1C	-19	7	9	1	2	57	51	-11	1	12	-26	10	-2	2	6	443	447
3	9	C	106	-110	-2	0	12	89	103	9	1	3	36	28	-11	1	13	129	-133	-2	2	7	89	73
3	11	C	144	-155	-2	0	14	55	-71	9	1	4	78	-69	-11	1	14	-26	-15	-2	2	8	298	-283
3	13	C	-26	-22	-4	0	2	588	532	9	1	5	-24	-4	-11	1	15	89	78	-2	2	9	147	-144
3	15	C	27	24	-4	0	4	146	-146	9	1	6	53	52	-11	1	16	28	-25	-2	2	10	154	192
4	0	C	354	-364	-4	0	6	76	-87	11	1	1	86	-81	-11	1	17	-14	-25	-2	2	11	137	140
4	2	C	377	-410	-4	0	8	517	473	11	1	2	84	-76	-13	1	1	31	-29	-2	2	12	35	-43
4	4	C	159	153	-4	0	10	57C	-555	11	1	3	-21	15	-13	1	2	115	95	-2	2	13	82	-83
4	6	C	114	54	-4	0	12	231	265	-1	1	1	496	-538*	-13	1	3	-26	3	-2	2	14	-2C	-8
4	8	C	-24	3	-4	0	14	58	-7C	-1	1	2	361	-325	-13	1	4	173	-156	-2	2	15	-13	32
4	10	C	37	32	-4	0	16	22	-33	-1	1	3	446	413	-13	1	5	39	-25	-4	2	2	538	553
4	12	C	-28	-8	-6	0	2	218	-255	-1	1	4	110	-86	-13	1	6	120	113	-4	2	3	88	-80
4	14	C	96	102	-6	0	4	716	617	-1	1	5	62	56	-13	1	7	78	68	-4	2	4	395	-412
5	1	C	278	-272	-6	0	6	1006	-1014	-1	1	6	67	63	-13	1	8	-27	-28	-4	2	5	167	131
5	3	C	51	-41	-6	0	8	891	764	-1	1	7	147	-140	-13	1	9	92	-90	-4	2	6	259	223
5	5	C	477	484	-6	0	10	151	-153	-1	1	8	68	-6C	-13	1	10	-28	-20	-4	2	7	85	86
5	7	C	42	40	-6	0	12	79	-102	-1	1	9	31	24	-13	1	11	1C7	1C2	-4	2	8	24	-13
5	9	C	32	21	-6	0	14	111	137	-1	1	10	148	-152	-13	1	12	55	45	-4	2	9	215	-192
5	11	C	107	-122	-6	0	16	27	-38	-1	1	11	46	43	-13	1	13	67	-61	-4	2	10	189	-167
5	13	C	-24	-26	-8	0	2	500	-490	-1	1	12	170	178	-13	1	14	51	-48	-4	2	11	154	133
6	C	C	8C	-78	-8	0	4	546	559	-1	1	13	63	-65	-13	1	15	29	25	-4	2	12	114	117
6	2	C	165	-155	-8	0	6	180	-158	-1	1	14	93	-101	-13	1	16	47	50	-4	2	13	-24	5
6	4	C	300	279	-8	0	8	225	-242	-3	1	1	124	-112	-15	1	4	-18	-7	-4	2	14	33	-35
6	6	C	136	135	-8	0	10	297	302	-3	1	2	-11	-34	-15	1	5	29	-23	-4	2	15	65	-65
6	8	0	130	-115	-8	0	12	169	-177	-3	1	3	259	-283	-15	1	6	3C	-22	-6	2	1	351	378
6	10	C	108	-1C2	-8	0	14	22	21	-3	1	4	-13	-4	-15	1	7	44	37	-6	2	2	73	73
6	12	C	94	-99	-8	0	16	-16	0	-3	1	5	111	117	-15	1	8	70	63	-6	2	3	166	-163
6	14	0	39	42	-1C	0	2	77	-85	-3	1	6	67	-7C	-15	1	9	66	-65	-6	2	4	145	126
7	1	C	263	-237	-10	0	4	37	-38	-3	1	7	167	143	-15	1	10	124	-119	-6	2	5	165	-167
7	3	C	122	-102	-10	0	6	118	144	-3	1	8	381	368	-15	1	11	59	59	-6	2	6	288	-274
7	5	C	197	182	-10	0	8	91	-117	-3	1	9	230	-206	-15	1	12	113	105	-6	2	7	331	331
7	7	0	46	-35	-1C	0	10	26	25	-3	1	10	195	-194	-15	1	13	29	-29	-6	2	8	243	217
7	9	0	42	36	-10	0	12	53	65	-3	1	11	162	165	-15	1	14	47	-47	-6	2	9	184	-175
7	11	C	4C	-33	-10	0	14	78	-102	-3	1	12	34	33	0	2	1	510	-503	-6	2	10	-23	2
7	13	C	5C	49	-1C	0	16	124	141	-3	1	13	74	-71	0	2	2	221	-242	-6	2	11	79	-76
8	C	0	228	219	-12	0	2	82	-P7	-3	1	14	60	56	0	2	3	-12	1	-6	2	12	103	-102
8	2	C	-25	-2	-12	0	4	61	66	-3	1	15	-20	11	0	2	4	43	34	-6	2	13	107	57
8	4	C	159	143	-12	0	6	31	-31	-5	1	1	45	53	0	2	5	316	329	-6	2	14	115	117
8	6	C	50	46	-12	0	8	38	47	-5	1	2	248	263	0	2	6	247	232	-8	2	1	134	-135
8	8	C	34	-26	-12	0	10	120	-151	-5	1	3	197	195	C	2	7	235	-213	-8	2	2	81	-80
8	10	C	-23	-2	-12	0	12	190	224	-5	1	4	111	-110	0	2	8	171	-163	-8	2	3	243	351
8	12	C	59	-66	-12	0	14	191	-2C7	-5	1	5	421	-400	0	2	9	43	64	-8	2	4	-21	19
9	1	C	35	26	-12	0	16	58	72	-5	1	6	127	-104	0	2	10	66	65	-8	2	5	372	-411
9	3	C	132	-118	-14	0	2	15	-11	-5	1	7	405	395	0	2	11	57	65	-8	2	6	212	197
9	5	C	-26	-29	-14	0	4	25	-28	-5	1	8	136	-124	0	2	12	58	-54	-8	2	7	175	178
9	7	C	77	-66	-14	0	6	-18	-3	-5	1	9	273	-255	0	2	13	70	-73	-8	2	8	350	-339
9	9	C	98	81	-14	0	8	107	128	-5	1	10	1C3	103	2	2	1	443	-499	-8	2	9	43	43
9	11	0	-2C	8	-14	0	10	143	-164	-5	1	11	133	138	2	2	2	29	-27	-8	2	10	286	272
1C	0	0	165	151	-14	0	12	63	85	-5	1	12	97	-91	2	2	3	421	433	-8	2	11	-25	-18
10	2	C	71	-60	-14	0	14	25	34	-5	1	13	41	-39	2	2	4	2C0	203	-8	2	12	152	-155
1C	4	C	84	-76	-16	0	8	52	6C	-5	1	14	53	53	2	2	5	190	-194	-8	2	13	-25	-15
1C	6	C	104	-94	-16	0	10	14	-11	-5	1	15	-24	-13	2	2	6	149	-151	-8	2	14	75	73
1C	8	C	36	21	-16	0	12	-13	-21	-5	1	16	25	-23	2	2	7	101	-96	-8	2	15	3C	30
10	10	C	82	85	1	1	1	439	-522*	-7	1	1	200	-200	2	2	8	-25	-11	-8	2	16	96	-36
11	1	C	222	211	1	1	2	263	271	-7	1	2	149	160	2	2	9	178	185	-10	2	1	238	-230
11	3	C	-26	4	1	1	3	476	455	-7	1	3	295	322	2	2	10	37	37	-10	2	2	179	162
11	5	C	47	-30	1	1	4	146	-154	-7	1	4	-19	-6	2	2	11	96	-98	-10	2	3	2C7	218
11	7	C	101	-50	1	1	5	276	-293	-7	1	5	319	-349	2	2	12	-19	-3	-10	2	4	261	-265
11	9	C	25	18	1	1	6	256	269	-7	1	6	43	-30	4	2	1	105	-97	-10	2	5	75	-74
12	C	C	63	50	1	1	7	83	86	-7	1	7	223	219	4	2	2	462	514	-10	2	6	253	255
12	2	C	77	-51	1	1	8	159	-163	-7	1	8	194	196	4	2	3	286	313	-10	2	7	32	-38
12	4	C	48	-37	1	1	9	31	1C	-7	1	9	144	-145	4	2	4	261	-277	-10	2	8	135	-142
12	6	C	49	-44	1	1	10	120	124	-7	1	10	109	-112	4	2	5	277	-276	-10	2	9	79	71
13	1	C	-15	0	1	1	11	-27	-13	-7	1	11	-26	1	4	2	6	77	85	-10	2	10	111	119
13	3	C	38	-33	1	1	12	32	-32	-7	1	12	33	19	4	2	7	168	179	-10	2	11	77	-76
C	0	2	132C	-1138*	1	1	13	-17	-3	-7	1	13	82	78	4	2	8	-24	4	-10	2	12	43	-45
0	0	4	344	291	3	1	1	188	-219	-7	1	14	-27	20	4	2	9	58	-58	-10	2	13	-24	24
C	0	6	155	151	3	1	2	599	-663	-7	1	15	44	-37	4	2	10	-21	4	-10	2	14	-24	1
C	C	8	147	-168	3	1	3	254	271	-7	1	16	-22	8	4	2	11	26	-34					
C	0	10	-19	14	3	1	4	277	315	-9	1	1	138	-144	6	2	1	230	226					
C	0	12	-17	16	3	1	5	221	-253	-9	1	2	241	-245	6	2	2	61	60					

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)
-10	2	15	27	24	7	3	2	103	56	-7	3	13	234	233	2	4	1	86	80	-6	4	3	453	-486
-10	2	16	42	41	7	3	3	184	-171	-7	3	14	54	-47	2	4	2	38	43	-6	4	4	159	-160
-12	2	1	54	-54	7	3	4	59	-54	-7	3	15	150	-138	2	4	3	36	31	-6	4	5	200	194
-12	2	2	50	42	7	3	5	101	78	-7	3	16	-24	6	2	4	4	50	-58	-6	4	6	-24	8
-12	2	3	-24	-8	7	3	6	-33	26	-9	3	1	38	40	2	4	5	30	24	-6	4	7	44	-33
-12	2	4	-25	-28	7	3	7	-29	4	-9	3	2	107	95	2	4	6	104	-115	-6	4	8	32	32
-12	2	5	86	94	7	3	8	-20	-17	-9	3	3	33	25	2	4	7	207	-225	-6	4	9	61	46
-12	2	6	-25	11	9	3	1	77	79	-9	3	4	-29	-25	2	4	8	137	140	-6	4	10	75	-60
-12	2	7	168	-165	9	3	2	44	44	-9	3	5	45	42	2	4	9	212	239	-6	4	11	150	-133
-12	2	8	47	-52	9	3	3	54	-55	-9	3	6	115	-114	2	4	10	113	-115	-6	4	12	121	110
-12	2	9	102	105	9	3	4	34	-24	-9	3	7	225	-227	2	4	11	104	-105	-6	4	13	128	117
-12	2	10	25	0	9	3	5	52	44	-9	3	8	102	88	2	4	12	48	49	-6	4	14	88	-73
-12	2	11	30	27	9	3	6	-18	11	-9	3	9	440	420	4	4	1	81	-82	-6	4	15	32	-22
-12	2	12	53	55	11	3	1	-30	-18	-9	3	10	70	-63	4	4	2	62	63	-6	4	16	26	28
-12	2	13	58	-104	11	3	2	-29	14	-9	3	11	298	-309	4	4	3	70	78	-8	4	1	79	71
-12	2	14	66	-65	11	3	3	48	-46	-9	3	12	35	33	4	4	4	111	-106	-8	4	2	-28	-20
-12	2	15	91	92	-1	3	1	277	-257	-9	3	13	88	83	4	4	5	116	-114	-8	4	3	134	134
-12	2	16	-18	11	-1	3	2	275	248	-9	3	14	-31	15	4	4	6	121	129	-8	4	4	85	-87
-14	2	2	-17	15	-1	3	3	161	-140	-9	3	15	55	62	4	4	7	101	99	-8	4	5	145	-139
-14	2	3	68	-76	-1	3	4	-17	-1	-9	3	16	-25	-14	4	4	8	-31	-17	-8	4	6	32	23
-14	2	4	30	-39	-1	3	5	581	560	-11	3	1	64	-54	4	4	9	-30	-20	-8	4	7	-28	-3
-14	2	5	95	87	-1	3	6	155	-137	-11	3	2	35	-5	4	4	10	35	-30	-8	4	8	-29	7
-14	2	6	57	58	-1	3	7	596	-595	-11	3	3	-32	-24	6	4	1	256	264	-8	4	9	52	43
-14	2	7	25	22	-1	3	8	31	30	-11	3	4	-32	28	6	4	2	202	-215	-8	4	10	116	-105
-14	2	8	29	-25	-1	3	9	296	296	-11	3	5	206	197	6	4	3	43	-58	-8	4	11	71	0
-14	2	9	126	-135	-1	3	10	53	-48	-11	3	6	39	40	6	4	4	37	28	-8	4	12	71	68
-14	2	10	-23	-4	-1	3	11	35	-25	-11	3	7	277	-280	6	4	5	-32	-20	-8	4	13	37	-29
-14	2	11	151	152	-1	3	12	34	27	-11	3	8	55	-48	6	4	6	39	31	-8	4	14	35	-21
-14	2	12	-22	-29	-1	3	13	64	-55	-11	3	9	88	80	6	4	7	37	37	-8	4	15	33	26
-14	2	13	94	-83	-1	3	14	-21	-5	-11	3	10	55	51	6	4	8	68	-60	-8	4	16	26	-20
-14	2	14	79	80	-3	3	1	694	791	-11	3	11	78	86	6	4	9	21	-24	-10	4	1	137	-125
-14	2	15	-16	-5	-3	3	2	142	-148	-11	3	12	56	-95	8	4	1	301	283	-10	4	2	106	108
-16	2	7	77	96	-3	3	3	1192	-1222	-11	3	13	135	-134	8	4	2	156	-159	-10	4	3	78	70
-16	2	8	40	-39	-3	3	4	287	267	-11	3	14	85	86	8	4	3	223	-233	-10	4	4	46	-47
-16	2	9	74	-73	-3	3	5	880	763	-11	3	15	78	72	8	4	4	132	139	-10	4	5	41	29
-16	2	10	56	51	-3	3	6	33	-49	-11	3	16	76	-68	8	4	5	108	105	-10	4	6	36	-22
-16	2	11	20	19	-3	3	7	179	-158	-13	3	1	34	24	8	4	6	53	-45	-10	4	7	36	-29
-16	2	12	47	-65	-3	3	8	-26	16	-13	3	2	39	36	8	4	7	19	-16	-10	4	8	138	139
1	3	1	542	-572	-3	3	9	191	-173	-13	3	3	108	-95	10	4	1	105	-92	-10	4	9	74	76
1	3	2	534	560	-3	3	10	78	63	-13	3	4	67	-61	10	4	2	-30	-11	-10	4	10	101	-96
1	3	3	308	313	-3	3	11	166	156	-13	3	5	94	90	10	4	3	-27	-3	-10	4	11	140	-140
1	3	4	454	-443	-3	3	12	90	-87	-13	3	6	70	55	10	4	4	44	40	-10	4	12	58	53
1	3	5	99	-96	-3	3	13	34	-29	-13	3	7	-30	2	12	4	1	-24	-7	-10	4	13	110	107
1	3	6	195	184	-3	3	14	66	62	-13	3	8	75	-68	-2	4	1	161	167	-10	4	14	-30	11
1	3	7	-28	-16	-3	3	15	-21	-12	-13	3	9	62	-38	-2	4	2	135	-152	-10	4	15	60	-53
1	3	8	-30	-18	-5	3	1	531	622	-13	3	10	103	105	-2	4	3	119	-109	-10	4	16	-23	-20
1	3	9	135	127	-5	3	2	31	-40	-13	3	11	38	31	-2	4	4	247	231	-12	4	1	-30	12
1	3	10	15	21	-5	3	3	119	-107	-13	3	12	74	-83	-2	4	5	48	-35	-12	4	2	-31	-14
1	3	11	105	-95	-5	3	4	255	-218	-13	3	13	-29	4	-2	4	6	179	-166	-12	4	3	84	-66
1	3	12	-25	-8	-5	3	5	276	-257	-13	3	14	39	37	-2	4	7	139	125	-12	4	4	98	90
1	3	13	28	26	-5	3	6	333	301	-13	3	15	27	-20	-2	4	8	-27	13	-12	4	5	123	123
3	3	1	107	120	-5	3	7	439	400	-13	3	16	-16	14	-2	4	9	76	-64	-12	4	6	161	-166
3	3	2	44	-43	-5	3	8	372	-340	-15	3	4	42	-12	-2	4	10	87	78	-12	4	7	213	-226
3	3	3	168	165	-5	3	9	251	-219	-15	3	5	32	44	-2	4	11	-32	22	-12	4	8	123	124
3	3	4	126	-127	-5	3	10	245	239	-15	3	6	42	29	-2	4	12	73	-74	-12	4	9	220	234
3	3	5	95	-96	-5	3	11	59	46	-15	3	7	41	-41	-2	4	13	34	-27	-12	4	10	83	-81
3	3	6	168	156	-5	3	12	112	-106	-15	3	8	30	-40	-2	4	14	40	33	-12	4	11	98	-95
3	3	7	37	-37	-5	3	13	-30	14	-15	3	9	-28	15	-4	4	1	96	-82	-12	4	12	-31	-1
3	3	8	88	-95	-5	3	14	-30	6	-15	3	10	-28	15	-4	4	2	256	-256	-12	4	13	-29	-16
3	3	9	33	31	-5	3	15	51	-43	-15	3	11	-26	-4	-4	4	3	215	-196	-12	4	14	-28	9
3	3	10	-25	18	-5	3	16	22	12	0	4	1	201	215	-4	4	4	196	194	-12	4	15	36	37
3	3	11	25	-21	-7	3	1	86	-84	0	4	2	105	-92	-4	4	5	261	267	-14	4	2	75	-69
5	3	1	557	565	-7	3	2	297	306	0	4	3	335	-346	-4	4	6	94	-83	-14	4	3	114	-102
5	3	2	31	-40	-7	3	3	166	156	0	4	4	240	242	-4	4	7	202	-197	-14	4	4	116	98
5	3	3	206	-201	-7	3	4	365	-361	0	4	5	480	502	-4	4	8	53	-55	-14	4	5	154	130
5	3	4	74	62	-7	3	5	220	-209	0	4	6	254	-244	-4	4	9	96	85	-14	4	6	90	-68
5	3	5	35	-26	-7	3	6	319	305	0	4	7	292	-291	-4	4	10	37	39	-14	4	7	62	-59
5	3	6	-32	-16	-7	3	7	80	72	0	4	8	183	188	-4	4	11	-32	-10	-14	4	8	33	27
5	3	7	58	60	-7	3	8	94	-55	0	4	9	-31	18	-4	4	12	-31	15	-14	4	9	84	-57
5	3	8	-30	1	-7	3	9	79	66	0	4	10	59	-53	-4	4	13	58	53	-14	4	10	42	36
5	3	9	-27	15	-7	3	10	33	-22	0	4	11	52	54	-4	4	14	69	-63	-14	4	11	104	92
5	3	10	-15	11	-7	3	11	219	-209	0	4	12	32	-22	-4	4	15	94	-89	-14	4	12	31	-27
7	3	1	81	78	-7	3	12	78	71	0	4	13	39	-40	-6	4	1	548	587	-14	4	13	37	-36
															-6	4	2	244	-263	-14	4	14	-22	6

The atomic scattering factors for selenium were corrected for anomal dispersion according to Cromer.[12]

Atomic parameters used to calculate the structure factors of Table 1, are listed in Tables 2 and 3, whereas the final bond lengths and angles are listed in Table 4.

Table 2. Final atomic coordinates from the least squares refinement. The coordinates are given in fractions of cell edges, and represent one asymmetric unit *i.e.* half a molecule.

	x	y	z
Se_1	0.0000	0.2135	0.2500
Se_2	0.0919	0.0971	0.1830
Se_3	0.3597	−0.0442	0.2842
P	0.2851	0.0624	0.3487
C_1	0.2704	0.0143	0.4683
C_2	0.2134	−0.0988	0.4469
C_3	0.3686	0.1897	0.4086
C_4	0.4156	0.2405	0.3385

Table 3. Final temperature factors $\beta_{ij} \times 10^3$. 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}
Se_1	9.28	6.64	12.50	0.00	13.70	0.00
Se_2	8.45	8.27	8.42	0.54	9.89	1.03
Se_3	12.25	9.55	10.77	−0.43	14.41	5.91
P	8.26	5.75	7.78	1.77	10.08	1.26

For the carbon atoms a temperature factor $\exp-B(\sin^2\theta/\lambda^2)$ was used with $B=4.89$, 6.55, 5.62, and 8.54 for C_1, C_2, C_3, and C_4, respectively.

Table 4. Bond lengths and angles with standard deviations in the selenium bis(diethyl-diselenophosphinate) molecule.

Se_1-Se_2	2.352 ± 0.002 Å	$\angle Se_2'-Se_1-Se_2$	103.9 ± 0.2
Se_2-P	2.239 ± 0.007	$\angle Se_1-Se_2-P$	105.0 ± 0.2
$P-Se_3$	2.095 ± 0.006	$\angle Se_2-P-Se_3$	103.1 ± 0.3
$P-C_1$	1.82 ± 0.02	$\angle Se_2-P-C_1$	108.7 ± 0.9
$P-C_3$	1.83 ± 0.03	$\angle Se_2-P-C_3$	108.2 ± 1.1
C_1-C_2	1.54 ± 0.04	$\angle Se_3-P-C_1$	117.3 ± 0.9
C_3-C_4	1.52 ± 0.03	$\angle Se_3-P-C_3$	115.9 ± 0.7
		$\angle C_1-P-C_3$	103.3 ± 1.8
		$\angle P-C_1-C_2$	114.5 ± 1.8
		$\angle P-C_3-C_4$	115.7 ± 2.0

The dihedral angle $Se_2'Se_1Se_2/Se_1Se_2P$ is $92.5 \pm 0.5°$.

Primes are used to denote atoms in one half of the molecule related to the other half (Table 2) by a twofold symmetry axis parallel to b through Se_1.

THE STRUCTURE OF THE SELENIUM BIS(DIETHYLDISELENO-PHOSPHINATE) MOLECULE AND THE CONFIGURATION AROUND THE CENTRAL SELENIUM ATOM

The final electron density projections along b and c are shown in Figs. 1 and 2. In Fig. 3, the molecule is seen projected onto the 001 plane. Bond lengths and angles are also shown in this figure. In addition, Fig. 3 illustrates the tendency to square-planar coordination around the central selenium
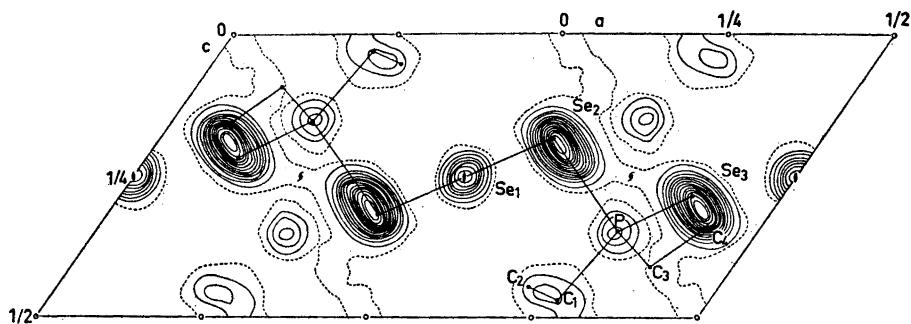
Fig. 1. Electron density projection of selenium bis(diethyldiselenophosphinate) along the b axis. Contour intervals at $3e^-/Å^2$ for C_1 and C_2, and at $6e^-/Å^2$ for the other atoms. Lowest contour (dashed) at $6e^-/Å^2$.
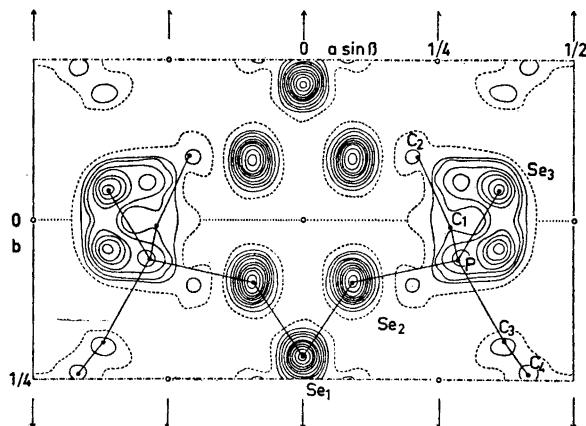
Fig. 2. Electron density projection of selenium bis(diethyldiselenophosphinate) along the c axis. Contour intervals at $3e^-/Å^2$ for C_2, C_3 and C_4, and at $6e^-/Å^2$ for the other atoms. Lowest contour (dashed) at $6e^-/Å^2$.

atom; two selenium atoms belonging to neighbour molecules are shown in the figure.

Each central selenium atom is surrounded by four ligand selenium atoms. In the resulting $SeSe_4$ group, two of the ligand atoms belong to the molecule proper while the two other belong to neighbour molecules. The $SeSe_4$ group is very similar to the corresponding $TeSe_2S_2$ group in tellurium bis(diethylthioselenophosphinate).[6] A least squares plane through the $SeSe_4$ group obeys the equation $0.272X + 0.962Z = 2.124$, where X and Z are the coordinates in Å units with respect to an orthogonal coordinate system, where the Z axis is put normal to the crystallographic a and b axes. The distances of the atoms of the $SeSe_4$ group from this plane is $Se_1 = 0.00$ Å, $Se_2 = 0.25$ Å, $Se_2' = -0.25$ Å,
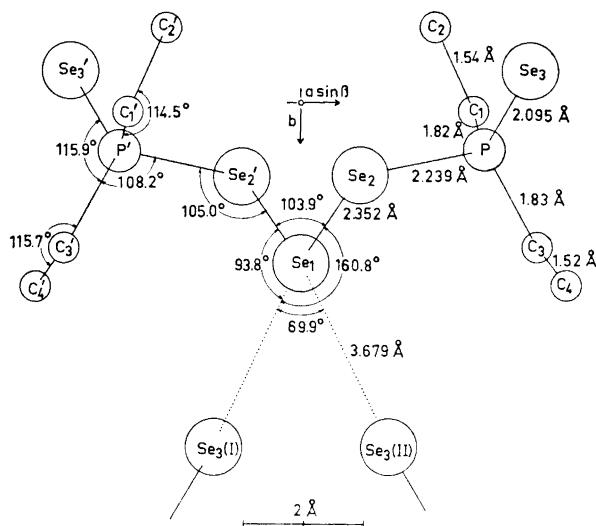
Fig. 3. The selenium bis(diethyldiselenophosphinate) molecule and the configuration around Se_1 seen along *c*. (I) and (II) indicate atoms in molecules which are generated from the original one by the screw axes $(-1/4, y, 1/4)$ and $(1/4, y, 1/4)$, respectively. Primed letters denote atoms in half the molecule related to the other half (Table 2) by a twofold symmetry axis through Se_1.

$Se_3(I) = 0.20$ Å and $Se_3(II) = -0.20$ Å. Here I and II indicate atoms in molecules which are related to the original one (Table 2) by the screw axes $(-1/4,y,1/4)$ and $(1/4,y,1/4)$, respectively.

The corresponding intermolecular $Se_1\cdots Se_3$ contacts are both 3.68 Å, as compared to 4.00 Å for a van der Waals contact between two selenium atoms.[13] This short contact indicates that there is a weak, intermolecular Se—Se bonding effect. On basis of the above considerations and from bond lengths and angles (*cf.* Fig. 3) the compound can be considered a very distorted square-planar complex of divalent selenium. By comparison with the isomorphous compound, tellurium bis(diethylthioselenophosphinate),[6] one finds that the two structures, as might be expected, are very similar.

The $P'—Se_2'—Se_1—Se_2—P$ chain in the molecule has the *trans* configuration exhibited also by other phosphorus-containing compounds in this study.[3,6] As in the crystals of those compounds, the molecules also here occur in two enantiomorphous forms. One might well compare the triselenide part of the molecule, $—Se_2'—Se_1—Se_2—$, with a partial selenium chain in elementary trigonal selenium [14] (Table 6). The $—Se_1—Se_2—P—Se_3$ group is almost planar, all atoms of that group being within 0.015 Å from the least squares plane.

Some interplanar angles are: $Se_1Se_2PSe_3/Se_1Se_2Se_2'Se_3(I)Se_3(II) = 87.6°$, $Se_1Se_2PSe_3/PC_1C_3 = 89.5°$, and $Se_1Se_2PSe_3/Se_2PSe_3 = 0.8°$. For the dihedral angle $Se_2'Se_1Se_2/Se_1Se_2P$ a value of 92.5° is found.

Table 5. Some other interatomic distances and angles.

Se_1-P	3.64 Å		$\angle Se_2-Se_1-Se_3(II)$	$93.8 \pm 0.3°$
Se_1-C_1	3.90		$\angle Se_2-Se_1-Se_3(I)$	160.8 ± 0.3
Se_1-C_3	3.96		$\angle Se_3(I)-Se_1-Se_3(II)$	69.9 ± 0.3
Se_2-Se_3	3.40			
Se_2-C_1	3.31			
Se_2-C_2	3.82			
Se_2-C_3	3.30			
Se_2-C_4	3.88			
Se_3-C_1	3.35			
Se_3-C_2	3.67			
Se_3-C_3	3.33			
Se_3-C_4	3.61			
$P-C_2$	2.83			
$P-C_4$	2.84			
Se_2-Se_2'	3.71			
$Se_1-Se_3(I)$	3.679 ± 0.004			

Packing of molecules. The packing of the molecules in the crystal is shown in Fig. 4. Dotted lines in the figure indicate the intermolecular $Se_1 \cdots Se_3$ contacts. As mentioned before, there are two such contacts per Se_1 atom. They connect
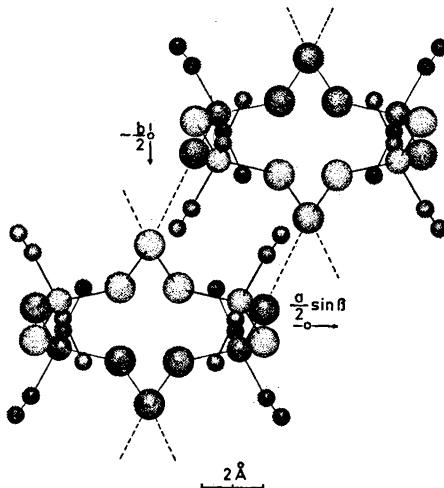
Fig. 4. The molecular arrangement of selenium bis(diethyldiselenophosphinate) seen along the c axis. Dashed lines indicate short intermolecular $Se_1 \cdots Se_3$ contacts.

the molecules into two-dimensional sheets parallel to the 001 plane. Other especially short intermolecular contacts were not found, but there are several intermolecular $C \cdots C$ separations around 4 Å.

Molecular dimensions. The length of the Se_1-Se_2 bond is found to be 2.352 ± 0.002 Å. This length is a little larger than the Se—Se bond length based on Pauling's covalent radius for selenium, 1.17 Å. Recent crystallo-

Table 6. Some selected Se—Se bond lengths and selenium valency angles.

Compound	Se—Se bond length (Å)	Se valency angle (°)
Bis(diethylthiophosphoryl) diselenide [18]	2.334 ± 0.012	106.2 ± 0.5
Tellurium bis(diethylthioseleno-phosphinate) [6]		104.7 ± 0.3
Selenium bis(diethyldiselenophosphinate)	2.352 ± 0.002	103.9 ± 0.2
		105.0 ± 0.2
Trigonal selenium [14]	2.373 ± 0.05	103.1 ± 0.2
α-Monoclinic selenium [19]	2.318	105.9
β-Monoclinic selenium [20]	2.34 ± 0.02	105.7 ± 0.8
Diphenyl diselenide [21]	2.29 ± 0.01	106 ± 2
Perfluoromethyldiselenide [22]	2.335 ± 0.032	
1,2-Diselenane-3,6-dicarboxylic acid [23]	2.332 ± 0.007	
Racem-1,2-diselenane-3,6-dicarboxylic acid [24]	2.321 ± 0.015	95.7 ± 0.8
p′,p-Dichlorodiphenyl diselenide [25]	2.333 ± 0.15	101.1 ± 0.6
Selenium diselenocyanate [7]	2.33	101
		95

Table 7. Some recently determined P—Se, P=S and P=Se bond lengths (in Å).

Compound	P—Se	P=S	P=Se
Tellurium bis(dimethyldithio-phosphate) [3]		1.923 ± 0.007	
Bis(diethylthiophosphoryl) diselenide [18]	2.275 ± 0.011	1.932 ± 0.011	
Tellurium bis(diethylthio-selenophosphinate) [6]	2.258 ± 0.010	1.926 ± 0.011	
Selenium bis(diethyldi-selenophosphinate)	2.239 ± 0.007		2.095 ± 0.006
Tetraethyl diphosphine disulphide [26]		1.94 ± 0.01	
Metadithiophosphonate [27]		1.945 ± 0.005	
Potassium dimethyl dithiophosphate [28]		1.960 ± 0.013 [a]	

[a] Intermediate between a single and a double bond.

graphic investigations by Cherin and Unger on trigonal selenium [14] show a Se—Se bond length of 2.373 ± 0.005 Å, which is larger than the value found in the present work. In both cases, there is a short intermolecular Se···Se contact *trans* to the Se—Se bond. From studies by Krebs,[15,16] it follows that such *trans* contacts have a lengthening effect on the Se—Se bond.

The close $Se_1···Se_3$ contacts occur in a roughly linear $Se_1—Se_2···Se_3$ system with a $Se_1—Se_2···Se_3$ angle of 160.8° (Table 5). This system is quite analogous to the corresponding Se—Te···S system in tellurium bis(diethylthioseleno-phosphinate), and the bonding might thus be explained in a similar manner, *i.e.* on basis of three-center bonding, using *p*-orbitals on the respective atoms.

The $P-Se_2$ bond length of 2.239 Å is the same as the sum of covalent radii of phosphorus and selenium corrected for bond polarity.[17] It is shorter than the $P-Se$ bond length of 2.275 Å found in bis(diethylthiophosphoryl) diselenide, but this difference is not significant. The $P=Se_3$ double bond length of 2.095 Å is in good agreement with the expected value of 2.07 Å based on the covalent double bond radii for the two atoms. The $P-C$ and $C-C$ bond lengths are within the error limits equal to normal, covalent bonds.

For the angles on the central selenium atom, the following values were found: $\angle Se_2'-Se_1-Se_2=103.9°$, $\angle Se_2-Se_1-Se_3(II)=93.8°$, $\angle Se_3(I)-Se_1-Se_3(II)=69.8°$ and $\angle Se_2-Se_1-Se_3(I)=160.8°$. In addition to the $Se_2'-Se_1-Se_2$ angle, there is another selenium valency angle, $\angle Se_1-Se_2-P$ which is 105.0°. From Table 6 it is seen that these valency angles compare well with other selenium angles found earlier in this study and elsewhere. The bond angles on the phosphorus atom are in good agreement with those found earlier.[3,6,18] The average angle is 109.4°, corresponding to tetrahedral hybridization on the phosphorus atom, but as with other compounds in these studies,[3,6,18] the $Se_3=P-C_1$ and $Se_3=P-C_3$ angles are both larger than 115°, while the other bond angles on phosphorus are less than 109°.

In Tables 6 and 7, relevant data for bond lengths and angles in other compounds are collected, for comparison with selenium and tellurium complexes with phosphorus-containing ligands investigated in this laboratory. Some of the standard deviations quoted in those tables are probably too optimistic, as uncertainties in cell constants have been disregarded. Infrared absorption data corresponding to some of the $P=S$ and $P=Se$ bonds listed in Table 7 have been published recently.[2,4]

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