Acta Cryst. (1966). **20**, 610

The Crystal Structure of Trimethylselenonium Iodide, $(CH_3)_3SeI$

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(*Received* 19 *July* 1965)

Crystals of trimethylselenonium iodide, $(CH_3)_3SeI$ are orthorhombic, with space group *Pnma*, cell dimensions $a=14{\cdot}078$, $b=8{\cdot}000$, and $c=6{\cdot}177$ Å (formal e.s.d. ~0·01 %), and four formula units in the cell. The structure was refined by a three-dimensional full-matrix least-squares procedure. The structure is built up of pairs of selenonium and iodide ions with a linear arrangement of $\mathrm{C{-}}\overset{|}{\underset{|}{\mathrm{Se}}}\cdots\mathrm{I}$, where C–Se = 1·962 ($\sigma=0{\cdot}023$) and Se–I = 3·776 ($\sigma=0{\cdot}002$). The other C–Se distances are 1·946 ($\sigma=0{\cdot}016$) Å. The mean value of the nearly equal C–Se–C angles is 98·5°.

Introduction

Both sulfur and selenium form stable 'onium' compounds of the type R_3SX or R_3SeX. The geometry of a sulfonium ion was established through the determination of the crystal structure of trimethylsulfonium iodide by Zuccaro & McCullough (1959). Only an incomplete study on one selenonium compound, triphenylselenonium chloride, appears to have been reported in the literature (McCullough & Marsh, 1950*a*). The Se–Cl distance of 3·6 Å indicates an ionic compound, but no other conclusions regarding the structure of the selenonium ion could be drawn from that study. It was therefore felt that an investigation of the crystal structure of a salt of this type was desirable. Among the several selenonium salts that were readily available, it was found that the trimethylselenonium iodide would be the most promising from a crystallographic point of view. It would also be of interest to compare two so closely related compounds, one with sulfur and one with selenium as the central atom.

Experimental

By cooling an alcoholic solution of trimethylselenonium iodide, crystals suitable for X-ray analysis were obtained in the form of colorless prisms, elongated in the direction of the *a* axis.

Although normally the substance is perfectly stable at room temperature, it was found that exposure to X-rays caused rapid decomposition unless the crystal was cooled below −15 °C.

For this reason only a set of comparatively poor *h*0*l* data was collected at room temperature.

All photographs used for determination of the cell dimensions and for three-dimensional intensity data were prepared with the crystals kept in the temperature range between −15° and −20 °C. The crystals were sealed in thin-walled glass capillaries.

Weissenberg and oscillation photographs indicated an orthorhombic unit cell. The following systematic extinctions were observed: 0*kl* with $k+l$ odd, *hk*0 with *h* odd. The space group is accordingly *Pnma* or $Pn2_1a$. The cell dimensions were determined by means of zero level 0*kl* and *h*0*l* Weissenberg photographs taken with unfiltered Cu radiation. Powder diagrams of KCl were superimposed on both ends of these films for calibration purposes. The 2θ values (based on $a=6{\cdot}2850$ Å for KCl at −15 °C) for about 100 reflections were used in a least-squares refinement of the lattice parameters. The program used was written by R. A. Sparks at UCLA. With the wavelenghts for Cu *K* radiation taken as $\alpha_1=1{\cdot}54050$, $\alpha_2=1{\cdot}54434$, and $\beta=1{\cdot}39217$ Å, the following results were obtained:

$$a=14{\cdot}078,\ b=8{\cdot}000,\ c=6{\cdot}177\ \text{Å}.$$

Formal e.s.d. ~0·01 %.

The density measured by flotation was 2·37 g.cm^{-3}, while that calculated for $Z=4$ is 2·396 g.cm^{-3}.

Integrated equi-inclination Weissenberg photographs of the layers with $l=0$ through 6, $k=0$ and 1, and $h=0$ were prepared by use of filtered Mo radiation, with tin foil interleaves between the films. About two-thirds of the intensities recorded were measured with a densitometer, while the weakest one-third was estimated visually by use of a calibrated integrated comparison strip. Of about 580 unique reflections that were recorded, the majority was observed in four different octants. The intensities were corrected for Lorentz and polarization effects in the usual way.

The crystals used were roughly cut to approximate a spherical shape with a diameter of about 0·1–0·15 mm. No absorption corrections were applied.

Solution and refinement of the structure

On the *c*-axis photographs it was noted that the intensity distribution was almost the same on all rows with

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k even, and likewise for the rows with k odd. This observation suggested that the heavy atoms were located in the mirror planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$ in *Pnma*. The solution of the structure was based on this assumption. The successful refinement of the structure indicates that the choice of space group was correct.

With the $h0l$ data collected at room temperature the Patterson function $P(U, W)$ was calculated. The I–Se vector nearly parallel to the c axis, with the end point at $U \sim 0{\cdot}01$ and $W \sim 0{\cdot}33$ was readily identified. However, there appeared to be four possible solutions, and instead of trying them out one after one, a search program written by R.A.Sparks for the IBM 7090 was used to move the identified I–Se vector across one asymmetric unit. For each position the weighted sum of $(F_o-F_c)^2$ was printed out. A scan of 2500 points required about the same amount of machine time as one two-dimensional Fourier synthesis. Four minima in the resulting table, corresponding to the four possible solutions of the Patterson function were observed. The I and Se positions derived from the deepest of these minima was used as input for a structure-factor Fourier-synthesis calculation. The resulting electron density projection clearly showed peaks corresponding to I, Se, one double C and one single C atom. The x, z parameters obtained were used as starting parameters for a two-dimensional least-squares refinement, which after a few cycles converged (with $R=0{\cdot}067$) towards a set of positional parameters which were essentially the same as the final ones for I, Se and the 'double' C atom, whereas the C atom in the mirror plane showed a deviation of a couple of tenths of an Å.

Assuming a Se–C distance of 1·95 Å, and an angle C–Se–C of 100°, the y coordinate for the C atom not situated in a mirror plane was calculated.

Using the complete set of three-dimensional data, eight cycles of full-matrix least-squares refinement were performed. Following cycle three, anisotropic temperature factors for I and Se were introduced. It was not attempted to locate the hydrogen atoms, and they were not included in any calculations. Reflections too weak to be observed were not used in the least-squares refinement. The shifts in the last cycle were in no case greater than 1/20 of the corresponding standard deviation. The final parameters arrived at are given in Tables 1 and 2 together with their estimated standard deviations. The R index is 0·056 for all observed reflections. In Table 3 is given a comparison of observed and calculated structure factors. The F_c's were calculated from the final parameters given in Tables 1 and 2. Unobserved reflections, indicated by U, are included in the table, with an F_o corresponding to the minimum observable intensity.

Table 1. *Final positional parameters and their standard deviations*

The e.s.d. (in parentheses) have been multiplied by 10^4.

Atom	x	y	z
I	0·0922 (0·8)	0·75	0·4027 (2)
Se	0·0794 (1·2)	0·25	0·0672 (3)
C(1)	0·1705 (16)	0·25	0·3075 (37)
C(2)	0·1334 (10)	0·0649 (20)	−0·0961 (27)

Table 2. *Final thermal parameters* (Å²) *and their standard deviations*

The e.s.d. (in parentheses) have been multiplied by 10^3. The relation between the B's given below and the β's in the anisotropic temperature factor expression is given by $B_{11}=4a^2\beta_{11}$, $B_{13}=2ac\beta_{13}$ *etc.*

Atom	B_{11}	B_{22}	B_{33}	B_{13}
I	2·497 (46)	2·747 (52)	2·773 (58)	−0·269 (43)
Se	2·018 (66)	3·796 (92)	2·201 (83)	0·271 (56)
C(1)	3·51 (420)	(isotropic)		
C(2)	3·40 (254)	(isotropic)		

As a final check of the structure, a difference Fourier synthesis was calculated with all atoms subtracted. No disturbing features could be detected. The Fourier program used was one written by P.K.Gantzel and H.Hope at UCLA, and the least-squares program was ACA Computer Program No. 317 (UCLALS-1) written by P.K.Gantzel, R.A.Sparks and K.N.Trueblood; both programs were adapted for use on the UNIVAC 1107 computer. The least-squares program minimizes the weighted sum of the squares of $KF_o-G(F_c)$ by a full-matrix routine. Of the scale factors K and G, the latter is one of the adjustable parameters. The weighting scheme of Hughes (1941) was used with $4F_o(\min)=58$. The atomic form factors were those of Hanson, Herman, Lea & Skillman (1964). The isotropic temperature factors are of the form $\exp(-B\sin^2\theta/\lambda^2)$, the anisotropic of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

The R index is defined by $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$. The standard deviations were estimated from the inverse matrix of the normal equations.

Description of the structure

In Fig. 1 are shown two projections of the structure, along the c axis and the b axis. Interatomic distances are given in Table 4 and Fig. 1(b). Angles are given in Table 4.

An electron diffraction study of dimethyl selenide (Goldish, Hedberg, Marsh & Shoemaker, 1955) gave a C–Se distance of 1·977 Å, and a C–Se–C angle of 98°. Comparison with the distances and angles found in the present study shows that no great change has taken place in these parameters with the formation of the selenonium ion. Within the limits of error the two crystallographically nonequivalent C–Se distances are equal, and they do not differ significantly from the sum of the single covalent bond radii (1·94 Å). The two C–Se–C angles are also almost equal, so that there is no indication of a difference in bonding between the two equatorial C atoms on one side, and the axial C atom (situated in the mirror plane) on the other. As in the trimethylsulfonium ion (Zuccaro & McCullough, 1959) the symmetry closely approximates $3m$ if only the 'onium' ion is considered. However, if the position

Table 3. *Observed and calculated structure factors*

The data are separated into groups having common *k* and *l*. The three columns in each group list values of *h*, $10F_o$ and $10F_c$, in that order. For unobserved reflections, indicated by *U*, the minimum observable F_o is given.

K = 0, L = 0		
4	1909	-2062
6	1965	-2186
8	574	-541
10	1004	994
12	1122	1118
14	219	196
16	551	-475
18	430	-427
K = 1, L = 0		
4	504	421
6	563	-550
8	680	-689
10	179	188
12	619	647
14	322	306
16	280	-250
18	431	-406
K = 2, L = 0		
0	2846	-2906
2	1194	-1238
4	1289	1362
6	2009	2094
8	732	712
10	1004	-1011
12	1152	-1141
14	223U	-115
16	496	491
18	360	360
K = 3, L = 0		
2	758	-735
4	336	-287
6	671	670
8	575	535
10	250	-250
12	546	-508
14	229	-229
16	249U	174
18	352	338
K = 4, L = 0		
0	2004	2214
2	859	894
4	1101	-1138
6	1553	-1591
8	558	-483
10	794	790
12	920	886
14	236U	102
16	421	-396
18	360	-306
K = 5, L = 0		
2	321	294
4	286	283
6	330	-297
8	488	-491
10	212U	54
12	435	444
14	245	247
16	264U	-161
18	369	-287
K = 6, L = 0		
0	1450	-1553
2	565	-565
4	805	842
6	1059	1067
8	246	270
10	556	-543
12	656	-597
14	256U	-77
16	273	263
18	291	232
K = 7, L = 0		
2	334	-330
4	206U	-199
6	251	268
8	296	329
10	238U	-54
12	294	-278
14	268U	-165
K = 8, L = 0		
0	798	816
2	364	362
4	434	-423
6	680	-680
8	242	-223
10	417	380
12	477	414
K = 9, L = 0		
2	239	236
4	243U	145
6	250U	-167
8	258U	-220
K = 10, L = 0		
0	522	-501
2	300	-192
4	342	265
6	440	366
K = 0, L = 1		
2	1366	-1353
3	235U	152
4	1024	-1016
5	377	368
6	114U	101
7	124U	45
8	896	915
9	483	-513
10	616	608
11	403	-416
12	198	-265
13	179	236
14	491	-489
15	493	487
K = 1, L = 1		
0	549	501
1	1380	-1405
2	328	240
3	2366	-2492
4	507	-467
5	872	-818
6	478	-465
7	1173	1139
8	158	237
9	1354	1349
10	401	409
11	349	311
12	171U	78
13	578	-566
14	169U	-193
15	613	-601
K = 2, L = 1		
1	519	453
2	1541	1476
3	532	-455
4	902	867
5	543	-502
6	296	-267
7	173	152
8	822	-791
9	526	524
10	412	-479
11	373	278
12	203	207
13	239	-223
14	390	418
15	408	-392
K = 3, L = 1		
0	140	-241
1	859	900
2	225	-204
3	1791	1845
4	245	246
5	843	835
6	415	430
7	921	-900
8	148U	-113
9	1235	-1257
10	391	-391
11	308	-278
12	160U	-116
13	507	559
14	196U	192
15	536	522
K = 4, L = 1		
1	255	-282
2	955	-993
3	251	248
4	673	-683
5	354	377
6	145U	165
7	151U	-35
8	660	647
9	444	-406
10	411	404
11	295	-277
12	187U	-185
13	195U	165
14	334	-355
15	347	342
K = 5, L = 1		
0	390	368
1	775	-798
2	143U	130
3	1296	-1416
4	358	-321
5	466	-439
6	321	-293
7	716	721
8	169U	154
9	803	825
10	161	269
11	188	181
12	196U	58
13	364	-367
14	211U	-118
15	359	-397
K = 6, L = 1		
1	157U	180
2	584	614
3	161U	-113
4	468	476
5	244	-264
6	171U	-84
7	176U	-50
8	459	-467
9	307	275
10	286	-302
11	199U	251
12	206U	150
13	213U	-99
14	287	269
15	264	-268
K = 7, L = 1		
0	226	-207
1	431	449
2	174U	-97
3	827	857
4	178U	173
5	325	330
6	185	222
7	452	-453
8	194U	-63
9	582	-584
10	205U	-204
K = 8, L = 1		
1	189	-198
2	453	-431
3	191U	134
4	318	-281
5	196U	230
6	199U	101
7	203U	-1
8	241	278
9	212U	-191
K = 9, L = 1		
0	204U	135
1	238	-254
2	205U	65
3	445	-490
4	209U	-107
5	211U	-192
6	214U	-140
7	253	270
8	222U	-29
9	372	349
K = 0, L = 2		
0	1290	1291
1	922	760
2	724	600
3	806	816
4	882	-828
5	371	-310
6	997	-1021
7	682	-682
8	323	-309
9	231	-225
10	356	344
11	321	358
12	460	471
13	418	445
14	241	211
15	193U	45
16	201U	-142
17	346	-280
K = 1, L = 2		
1	1660	-1644
2	74U	-32
3	84U	40
4	289	-267
5	1783	1768
6	114	-181
7	1264	1260
8	133U	14
9	391	-371
10	150	177
11	1027	-1033
12	195	249
13	446	-492
14	165U	46
15	253	256
16	202U	-177
17	458	434
K = 2, L = 2		
0	934	-1004
1	366	-363
2	644	-600
3	572	-547
4	463	453
5	113U	30
6	994	957
7	569	550
8	372	348
9	366	371
10	352	-346
11	513	-506
12	445	-469
13	423	-509
14	168U	-175
15	196U	-46
16	205U	148
17	312	309
K = 3, L = 2		
1	1609	1675
2	108U	-70
3	294	-229
4	270	216
5	1568	-1572
6	216	213
7	936	-933
8	145U	-21
9	378	358
10	187	-177
11	828	811
12	176	-198
13	397	417
14	192U	-29
15	233	-181
16	209U	139
17	358	-387
K = 4, L = 2		
0	758	803
1	367	379
2	453	440
3	529	511
4	388	-384
5	137U	-74
6	716	-731
7	501	-479
8	298	-252
9	266	-274
10	302	272
11	289	249
12	372	366
13	367	398
14	198U	142
15	206U	50
16	214U	-119
17	222	-238
K = 5, L = 2		
1	1009	-1055
2	140U	-15
3	143U	15
4	146U	-117
5	1024	1064
6	155U	-100
7	787	814
8	165U	-20
9	282	-243
10	178U	87
11	676	-706
12	192U	167
13	260	-318
14	206U	48
15	214U	200
16	221U	-112
17	300	298
K = 6, L = 2		
0	551	-564
1	335	-325
2	279	-287
3	410	-425
4	264	285
5	164U	85
6	466	489
7	374	374
8	206	153
9	183U	180
10	189U	-186
11	195	-177
12	263	-247
13	304	-273
K = 7, L = 2		
1	672	732
2	171U	-38
3	172U	-76
4	175U	61
5	680	-729
6	181U	87
7	443	-478
8	190U	21
9	195	185
10	200U	-58
11	419	440
12	212U	-104
13	218U	206
K = 8, L = 2		
0	304	305
1	165	151
2	243	173
3	245	246
4	189U	-145
5	192U	26
6	286	-304
7	260	-224
K = 9, L = 2		
1	386	-433
2	201U	41
3	202U	55
4	204U	-20
5	398	436
K = 0, L = 3		
1	446	537
2	1692	-1652
4	1668	-1644
5	436	-417
6	162	122
7	281	-342
8	1397	1410
9	113U	29
10	884	898
11	245	300
12	291	-278
13	141	142
14	662	-704
15	155U	-73
16	267	-306
17	169U	-84
18	176U	157
K = 1, L = 3		
0	516	567
1	52U	13
2	59U	34
3	122	87
4	563	-539
5	85U	-65
6	256	-254
7	239	-224
8	320	329
9	114U	5
10	446	475
11	168	190
12	135U	64
13	142U	115
14	342	-354
15	156U	-20
16	268	-301
17	170U	-114
18	176U	30
K = 2, L = 3		
1	559	-533
2	1778	1784
3	152	126
4	1481	1455
5	443	412
6	315	-301
7	259	276
8	1259	-1244
9	118U	-39
10	728	-726
11	301	-253
12	227	208
13	144	-129
14	599	607
15	158U	55
16	295	323
K = 3, L = 3		
0	334	-308
1	85U	13
2	87U	-63
3	91U	-56
4	310	310
5	100U	23
6	303	283
7	199	182
8	171	-174
9	123U	24
10	476	-466
11	177	-159
12	142	-124
13	146U	-117
14	315	340
15	161U	15
16	301	295
K = 4, L = 3		
1	418	397
2	1303	-1318
3	103U	-61
4	1147	-1153
5	349	-320
6	233	192
7	243	-230
8	1052	1017
9	150U	53
10	596	612
11	141	214
12	147	-195
13	153U	105
14	458	-514
15	166U	-53
16	252	-248
K = 5, L = 3		
0	442	438
1	112U	32
2	113U	48
3	115U	75
4	422	-400
5	121U	-45
6	205	-203
7	169	-152
8	271	221
9	138U	-2
10	342	322
11	149U	122
12	154U	58
13	160U	77
14	217	-219
K = 6, L = 3		
1	297	-261
2	813	851
3	127U	44
4	787	805
5	217	217
6	155U	-96
7	203	168
8	693	-736
9	147U	-25
10	425	-457
11	183	-161
12	162	167
13	167U	-71
14	351	390
K = 7, L = 3		
0	294	-255
1	137U	-16
2	137U	-58
3	139U	-51
4	232	221
5	143U	13
6	191	186
7	149U	100
8	153U	-92
9	157U	19
10	236	-252
K = 8, L = 3		
1	173	172
2	579	-602
3	151U	-43
4	465	-480
5	160	-144
6	157U	128
7	160U	-89
8	428	443
K = 9, L = 3		
0	161U	175
1	161U	13
2	162U	50
3	163U	38
4	164U	-141
K = 10, L = 3		
1	173U	-89
2	312	301
3	175U	18
4	297	276
K = 0, L = 4		
0	1070	-994
1	40U	36
2	329	-345
3	70U	12
4	658	647
5	265	-237
6	695	685
7	256	-272
8	117U	-15
9	125U	124
10	448	-459
11	331	325
12	349	-312
13	156U	157
14	163U	70
16	171U	-69
16	178	254
17	243	-199
K = 1, L = 4		
1	1162	-1182
2	607	-620
3	75U	73
4	505	-467
5	999	1011
6	195	197
7	859	863
8	500	515
9	126U	-37
10	134U	180
11	686	-676
12	284	-256
13	458	-447
14	252	-259
15	172U	76
16	179U	14
17	367	274
K = 2, L = 4		
0	762	771
1	77U	58
2	376	335
3	87U	51
4	519	-473
5	101U	121
6	719	-673
7	220	219
8	123U	-71
9	130U	-36
10	457	468
11	276	-288
12	327	340
13	159U	-195
14	166U	-96
15	174U	61
16	181	-261
17	188U	210
K = 3, L = 4		
1	1061	1065
2	668	640
3	182	-133
4	388	388
5	926	-906
6	264	-249
7	704	-679
8	451	-426
9	136U	54
10	143U	-113
11	565	546
12	205	202
13	357	382
14	170	208
K = 4, L = 4		
0	643	-666
1	109U	-3
2	289	-266
3	114U	5
4	421	422
5	122U	-115
6	535	538
7	154	-197
8	138U	32
9	144U	33
10	358	-375
11	204	231
12	310	-267
13	169	152
K = 5, L = 4		
1	723	-723
2	395	-390
3	127U	31
4	364	-320
5	672	637
6	138U	114
7	564	565
8	336	363
9	152U	-30
10	158U	141
11	449	-460
12	222	-187
13	258	-290
K = 6, L = 4		
0	477	514
1	137U	-39
2	181	186
3	140U	-51
4	341	-337
5	146U	92
6	367	-379
7	153U	163
8	157U	1
9	162U	-21
10	275	265
11	173U	-160
12	178U	184
K = 7, L = 4		
1	493	494
2	324	313
3	153U	-52
4	203	215
5	432	-435
6	161U	-113
7	346	-342
8	220	-244
9	173U	35
10	177U	-79
11	316	291
K = 8, L = 4		
0	214	-282
1	164U	6
2	165U	-125
3	166U	35
4	168U	174
5	170U	-12
K = 9, L = 4		
1	292	-291
2	176U	-202
3	179U	36
4	181U	-136
5	301	259
K = 0, L = 5		
1	243	341
2	385	-437
3	93U	-32
4	474	-489
5	479	-459
6	134U	-91
7	229	-243
8	266	322
9	263	295
10	325	360
11	295	340
12	198U	97
13	208U	-21
14	218U	-163
15	223	-251
16	237U	-203
K = 1, L = 5		
0	325	-395
1	593	636
2	197	-226
3	1065	1041
4	136	142
5	266	255
6	346	345
7	583	-576
8	190	206
9	658	-655
10	179U	-54
11	169U	-72
12	199U	-189
13	403	396
14	219U	-143
15	278	296
16	236U	-7
K = 2, L = 5		
1	408	-416
2	419	419
3	159	137
4	456	448
5	505	492
6	145U	71
7	165	137
8	290	-293
9	295	-303
10	324	-326
11	232	-255
12	203U	-94
13	212U	23
14	222U	147
15	232U	196
16	241U	192
K = 3, L = 5		
0	344	344
1	478	-477
2	187	189
3	892	-848
4	141U	-130
5	296	-295
6	312	-288
7	465	475
8	189	-166
9	640	632
10	191U	42
11	200U	70
12	209U	155
13	380	-390
14	227U	124
15	232	-261
16	246U	9
K = 4, L = 5		
1	321	324
2	339	-324
3	152U	-81
4	359	-353
5	412	-396
6	169U	-60
7	193	-151
8	265	234
9	214	243
10	240	261
11	250	241
12	217U	74
13	225U	-11
14	234U	-120
15	243U	-179
K = 5, L = 5		
0	321	-232
1	444	438
2	167U	-135
3	705	703
4	174U	82
5	178U	146
6	238	209
7	380	-399
8	197U	126
9	413	-424
10	211U	-33
11	219U	-39
12	226U	-116
13	230	267
14	243U	-87
K = 6, L = 5		
1	191	-224
2	240	215
3	167U	30
4	247	241
5	275	285
6	199U	44
7	204U	149
8	206	-161
9	212	-172
10	223	-182
11	230U	-209
K = 7, L = 5		
0	209	145
1	261	-265
2	202U	82
3	448	-452
4	207U	-54
5	211U	-130
6	215U	-126
7	263	263
8	224U	-74
9	309	319
10	236U	18
K = 8, L = 5		
1	227	194
2	220U	-132
3	222U	-61
4	224U	-141
5	236	-222
K = 9, L = 5		
1	211	159
2	237U	-42
3	286	275
K = 0, L = 6		
0	938	-912
1	214	-283
2	350	-398
3	508	-537
4	555	506
5	193	-186
6	767	721
7	273	284
8	101U	172
9	342	314
10	360	-346
11	122U	65
12	388	-388
13	134U	-126
14	141U	-92
15	147U	-145
16	227	187
K = 1, L = 6		
1	51U	34
2	149	-158
3	109	-102
4	74U	-50
5	81U	-77
6	159	142
7	96U	67
8	168	165
9	135	165
10	116U	-30
11	122U	95
12	129U	-202
13	135U	-104
14	141U	-110
15	147U	-165
16	153U	91
K = 2, L = 6		
0	727	763
1	212	230
2	382	379
3	479	475
4	403	-395
5	222	207
6	740	-695
7	261	-252
8	261	-215
9	303	-321
10	336	351
11	125U	-64
12	371	396
13	137U	138
14	143U	63
15	149U	135
16	155U	-192
K = 3, L = 6		
1	82U	-59
2	213	210
3	87U	114
4	92U	42
5	96U	88
6	214	-174
7	107U	-76
8	145	-135
9	118U	-151
10	124U	51
11	129U	-71
12	135U	162
13	141U	90
14	147U	85
15	152U	136
16	158U	-64
K = 4, L = 6		
0	652	-646
1	190	-197
2	329	-304
3	396	-393
4	477	347
5	158	-155
6	569	560
7	192	213
8	119U	156
9	249	253
10	310	-284
11	135U	47
12	294	-316
13	146U	-111
14	151U	-55
15	156U	-111
K = 5, L = 6		
1	107U	33
2	119	-114
3	110U	-61
4	113U	-61
5	116U	-63
6	119U	83
7	123U	26
8	127U	138
9	132U	110
10	136U	5
11	141U	80
12	146U	-146
13	151U	-64
14	156U	-94
K = 6, L = 6		
0	525	487
1	154	151
2	209	214
3	287	287
4	276	-274
5	145	98
6	365	-397
7	130	-161
8	136U	-92
9	181	-174
10	187	203
11	148U	-27
12	222	221
K = 7, L = 6		
1	130U	-44
2	131U	123
3	132U	53
4	134U	52
5	136U	60
6	139U	-81
7	142U	-19
8	145U	-101
9	148U	-80
10	152U	0
K = 8, L = 6		
0	252	-278
1	141U	-83
2	163	-140
3	208	-173
4	166	147
5	146U	-73
6	266	265

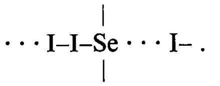
Table 4. *Interatomic distances and bond angles*

E.s.d. in parentheses

Atoms	Distance
Se–C(1)	1·962 (0·023) Å
Se–C(2)	1·946 (0·016)
I--Se	3·776 (0·002)
I′ -C(1)	4·173 (0·022)
I′ -C(2)	4·137 (0·014)
	Angle
C(1)-Se-C(2)	97·9°(0·7°)
C(2)-Se-C(2′)	99·1 (0·7)
C(1)-Se-I	178·9 (0·3)
C(2)-Se-I	81·5 (0·5)

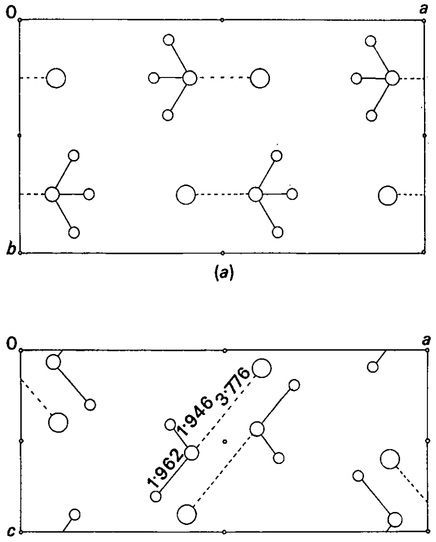
of the iodine atom relative to the selenonium group is taken into account it appears that this is not the true symmetry of the group. The iodine atom is situated in an axial position, at a distance of 3·78 Å from the Se atom. With a sum of van der Waals radii of 4·15 Å the observed interatomic distance, together with the atomic orientation, suggest the existence of a weak bond between selenium and iodine. It therefore seems reasonable to describe trimethylselenonium iodide as a charge transfer complex, with the iodide ion acting as donor, and the selenonium ion as acceptor.

It is interesting to compare this complex with the tetrahydroselenophene–iodine complex (Hope & McCullough, 1964) where a selenium–iodine bond of similar length (3·64 Å) and direction was found in the arrangement



$\cdots \mathrm{I{-}I{-}Se} \cdots \mathrm{I}^- .$

There is also a resemblance between the present selenonium salt and the compounds di-*p*-tolylselenium dichloride and di-*p*-tolylselenium dibromide (McCullough & Marsh, 1950*b*), where the halogen atoms occupy axial positions, while the organic groups occupy the equatorial positions. Apparently the selenonium iodide possesses some of the geometrical characteristics of four-bonded selenium compounds.



(*a*)

(*b*)

Fig. 1. (*a*) Projection of the structure of trimethylselenonium iodide along the *c* axis. The broken lines indicate an assumed Se–I bond. In order of decreasing size, the circles represent I, Se and C. (*b*) Projection along the *b* axis. The crystallographically independent bond distances are given.

Inspection of the thermal parameters reveals that the iodine atom vibrates very nearly isotropically, whereas the motion of the selenium atom is anisotropic with the largest component along the *b* axis. The reason for this, whether it indicates a slight disorder or not, is not known. Except for the Se–I distance, the packing distances are normal. An iodine atom rests against the three methyl groups, with one observed distance of 4·17 Å and two of 4·14 Å.

A comparison of the crystal structure of trimethylsulfonium iodide (Zuccaro & McCullough, 1959) with the present structure shows a striking similarity in the stacking of ions in the direction of the *b* axis [the central part of Fig. 1(*b*)]. It is interesting to note that even though the S–I distance of 3·89 Å is longer than the corresponding Se–I distance, it is still somewhat shorter than the sum of van der Waals radii (4·0 Å). With the similarity of the two structures in mind, it seems reasonable to assume that also in the trimethylsulfonium iodide we have a case of an ion–ion charge transfer complex.

Another example along the same lines is thiuret hydriodide. In the structure determination by Foss & Tjomsland (1958) an interionic S–I distance of only 3·62 Å was found. Hordvik & Sundsfjord (1965) have interpreted this as an indication of an ion–ion charge transfer bond.

The author is indebted to Professor J. D. McCullough for the gift of a sample of trimethylselenonium iodide, for his interest and many inspiring discussions, to Mr Tore Onstad for help with the intensity measurements, to the National Science Foundation for financial support under Grant NSF-G24997, to the Fulbright Foundation for a travel grant, to Norges almenvitenskapelige forskningsråd for financial support under Grant D. 302-46, and to the Norwegian Computing Center for the use of the UNIVAC 1107 computer.

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