The Crystal and Molecular Structure of *trans*-Bisdiethyl-selenidepalladium (II) Dichloride

POUL ERIK SKAKKE and SVEND ERIK RASMUSSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

The crystal structure of *trans*-dichloro-bis-(diethylselenide)palladium(II), [PdCl$_2$(Et$_2$Se)$_2$] was determined using automatically collected counter data. The structure was refined by least squares methods using 1046 reflexions to an R-value of 7.96 %. The space group is $P\bar{1}$ with $a=7.77$ Å, $b=6.97$ Å, $c=8.02$ Å, $\alpha=58.3°$, $\beta=91.4°$, $\gamma=92.4°$, and with one molecule per unit cell.

The configuration around the selenium is pyramidal. Palladium, selenium, and chlorine atoms are located in a planar arrangement. The molecule as a whole possesses a center of symmetry.

K. A. Jensen investigated the stereochemistry of divalent platinum and palladium complexes in the 1930's. Two important papers are Refs. 1 and 2. A review (in Danish) is given in Ref. 3. Jensen found that the pair of isomers, α- and β-[PtCl$_2$(Et$_2$Se)$_2$] and a number of analogous isomeric compounds PtX$_2$Y$_2$ were *cis-trans* isomers with the ligands in a planar arrangement around the central atom. He also found that the *trans*-dialkyl sulfide and dialkyl selenide compounds have a finite dipole moment of approximately 2.4 Debye and the molecules could not therefore be centrosymmetric. In order to obtain more definite information on the conformation around the ligands Professor Jensen suggested that we carried out an X-ray structure analysis on a test compound. A palladium complex was chosen in preference of a platinum compound in order to minimize absorption effects. Diethyl selenide was chosen as a ligand since the general knowledge of bond lengths in selenium compounds is less extensive than our knowledge about sulfur compounds.

During a search of the literature on palladium complexes of the type PdX$_2$Y$_2$ we did not find reports of complete crystal structure determinations on a pair of *cis-trans* isomers. All available papers on isomeric palladium compounds rely on indirect evidence for the assignment of geometric structures to alleged pairs of isomers.

EXPERIMENTAL

The crystals supplied by Professor Jensen are brownred, platy, opaque, and rather irregularly shaped. After some searching we found a crystal of a shape which would allow for a reasonable absorption correction. The part of the crystal which was bathed by the X-ray beam was a parallelepiped of dimensions $0.20 \times 0.25 \times 0.50$ mm^3. A lump of indefinite shape was attached to the parallelepiped. This lump of crystal was kept out of the X-ray beam. A sketch of the crystal is shown in Fig. 1.

Oscillation, Weissenberg, retigraph, and precession photographs were used to establish the size and shape of the unit cell. Intensities were measured using a linear diffractometer of the Arndt-Phillips [4] design. Mo-radiation was employed. Balanced filters, SrO, ZrO$_2$, in conjunction with a scintillation counter and a pulse height discriminator simulated a practically monochromatic MoKα beam. The diffractometer output was processed by a GIER computer, using an ALGOL program [5] which evaluated intensities, applied Lp-corrections, and gave the standard deviations. 1143 of the 1998 reflexions showed intensities greater than twice their standard deviation estimated as the square rooth of the total number of counts in an intensity measurement.

The photographs showed that the crystal was not of the best quality. Satellite spots were observed and an appreciable amount of diffuse scattering was discernible on photographs. A high accuracy was not to be expected.

STRUCTURE AND REFINEMENT

The X-ray photographs indicated a triclinic unit cell. The unit cell used in this paper was chosen from the following considerations: The direct axes were chosen parallel to the sides of the parallelpiped. The reciprocal axes a^* and b^* were perpendicular to the faces A and B on the crystal as shown on Fig. 1. The choice of the reciprocal c^* axis perpendicular to the face C of the crystal would result in a centered cell. We chose a c^* direction which gave a primitive cell and therefore arrived at a rather oblique cell of dimensions $a = 7.77$ Å, $b = 6.97$ Å, $c = 8.02$ Å, $\alpha = 58.3°$, $\beta = 91.4°$, $\gamma = 92.4°$. The data were corrected for absorption using a program by Wells [6] and brought on an approximate absolute scale using a Wilson plot program written by J. Danielsen.[7] An intensity statistic is given in Table 1. A centre of symmetry is clearly indicated. The density calculated for one formula unit per unit cell is 2.07 g/cm^3. Since the compound floats on CHBr$_3$ it has a density less than 2.8 g/cm^3. We found no suitable liquid for an exact density measurement but

Table 1. Statistical test for absence or presence of center of symmetry.

Normalized structure factors	Theoretical value for centrosymmetric space groups	Theoretical value for non centrosymmetric space groups	Computed values for PdCl$_2$(Et$_2$Se)$_2$
$\langle |E| \rangle$	0.798	0.886	0.767
$\langle |E|^2 \rangle$	1.000	1.000	1.026
$\langle |E|^2 - 1 \rangle$	0.968	0.736	1.027
No$|E| > 1(\%)$	32.0	36.8	33.6
No$|E| > 2(\%)$	5.0	1.8	3.8
No$|E| > 3(\%)$	0.3	0.01	0.55

believe that we can accept the hypothesis that there is one molecule PdCl$_2$(Et$_2$Se)$_2$ per unit cell. As no piezoelectric effect was detected by the Giebe-Scheibe method we found that we had enough evidence to assume that the space group is $P\bar{1}$ (No. 2). Precession photographs of [0kl] showed pronounced bands of strong reflections, probably correlated with Pd $-$ Se vectors. Only one Pd $-$ Se projected distance was found from the transforms indicating a center of symmetry around the palladium atom. A Fourier synthesis was calculated with all signs positive. The electron density map showed besides the origin peak two other peaks which were attributed to Se and Cl. After some refining including isotropic temperature factors for Pd, Se and Cl and positional parameters for the latter two atoms a difference Fourier synthesis revealed the locations of the four carbon atoms.
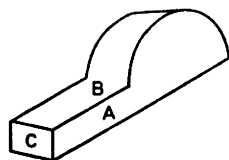

Fig. 1. Drawing of the crystal used in the X-ray investigation.
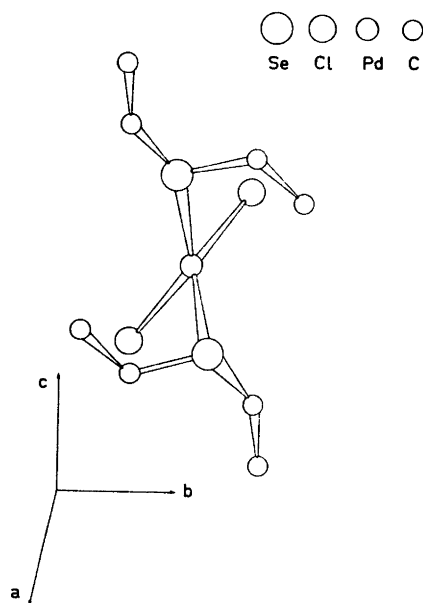
Fig. 2. Drawing of a Pd(Et$_2$Se)$_2$Cl$_2$ molecule.

The refinement was continued using the method of least-squares employing anisotropic temperature factor parameters. Atomic scattering factors were taken from *International Tables of Crystallography*, Vol. III, except for Pd for which the values of Cromer and Mann [8] were used. The scattering factors of Pd, Se, and Cl were corrected for anomalous dispersion effects using the values of Templeton and Dauben as published in *International Tables*. The weights employed were $w = 1/(\mu F)^2$ with $\mu F = \sqrt{F^2 + \sigma(F^2)} - |F|$. $\sigma(F^2) = \sigma(F^2)_{\text{count}} + aF^2$. $\sigma(F^2)_{\text{count}}$ is estimated from counting statistics and a was chosen so $(a = 0.06)$ that the weighted least-squares residual was independent of the size of F_o. In the last cycles of refinement reflections which were smaller

than 2·5 times their standard deviations were left out and some reflexions which were measured very close to the spindle axis of the diffractometer were also omitted as were some wrongly scaled reflexions on the ninth layer line. This left us with 1046 reflexions.

The least-squares programs used were G3,[9] which uses the block-diagonal approximation and ORFLS as incorporated in the X-ray-63 system.[10]

A plot of observed *versus* calculated structure factors gave no indication of extinction errors and a final difference Fourier synthesis revealed no higher

Table 2. Atomic parameters, coordinates in fractions of unit cell edges; standard deviations × 10^4 in parentheses.

	x	σx	y	σy	z	σz
Pd	0.0000	(0)	0.0000	(0)	0.0000	(0)
Se	0.2579	(2)	0.1221	(3)	−0.1904	(2)
Cl	0.1923	(6)	−0.1121	(9)	0.2598	(7)
C$_1$	0.3526	(21)	−0.1696	(28)	−0.1182	(27)
C$_2$	0.2226	(27)	−0.3199	(32)	−0.1547	(27)
C$_3$	0.1917	(25)	0.2324	(31)	−0.4612	(23)
C$_4$	0.3563	(29)	0.2918	(34)	−0.5783	(29)

Table 3. Temperature factor parameters. Root mean square values of principal axes of vibration ellipsoids in Å units.

	U_I	U_II	U_III
Pd	0.18	0.22	0.21
Se	0.20	0.21	0.24
Cl	0.20	0.31	0.22
C$_1$	0.17	0.24	0.29
C$_2$	0.33	0.25	0.20
C$_3$	0.30	0.25	0.18
C$_4$	0.32	0.29	0.17

Table 4. Bond lengths in Å units. Standard deviations × 10^3 in parentheses. Bond angles in degrees below.

Atoms	l	σl
Pd−Se	2.424	(7)
Pd−Cl	2.266	(9)
Se−C$_1$	1.960	(30)
Se−C$_3$	1.936	(42)
C$_1$−C$_2$	1.529	(68)
C$_3$−C$_4$	1.523	(68)

Atoms	Angles
Se−Pd−Cl	84.4
Pd−Se−C$_1$	100.8
Pd−Se−C$_3$	109.5
C$_1$−Se−C$_3$	99.1
Se−C$_1$−C$_2$	113.9
Se−C$_3$−C$_4$	108.9

Table 5. Observed and calculated structure factors.

h	k	l	Fo	Fc
-1	-7	0	97	114
0	-7	0	92	110
-1	-6	0	142	178
0	-6	0	74	77
2	-6	0	146	137
3	-6	0	184	186
6	-6	0	89	92
7	-6	0	102	92
-5	-5	0	114	161
-2	-5	0	232	269
-1	-5	0	187	196
0	-5	0	79	-68
1	-5	0	78	55
2	-5	0	319	316
3	-5	0	222	223
7	-5	0	119	109
-7	-4	0	64	54
-6	-4	0	143	203
-5	-4	0	119	125
-4	-4	0	95	-117
-3	-4	0	133	126
-2	-4	0	460	524
-1	-4	0	175	179
0	-4	0	135	-152
1	-4	0	181	178
2	-4	0	406	404
3	-4	0	211	201
5	-4	0	107	102
6	-4	0	182	186
9	-4	0	103	93
-7	-3	0	136	191
-6	-3	0	219	275
-5	-3	0	56	-35
-4	-3	0	103	-103
-3	-3	0	332	388
-2	-3	0	512	575
-1	-3	0	101	114
0	-3	0	60	-55
1	-3	0	431	390
2	-3	0	414	404
3	-3	0	56	31
4	-3	0	181	174
5	-3	0	335	338
6	-3	0	99	99
8	-3	0	86	79
9	-3	0	151	152
-7	-2	0	255	312
-6	-2	0	287	237
-5	-2	0	150	-156
-4	-2	0	94	112
-3	-2	0	523	599
-2	-2	0	362	413
-1	-2	0	79	68
1	-2	0	687	667
3	-2	0	120	-117
4	-2	0	439	410
5	-2	0	512	485
8	-2	0	169	151
9	-2	0	173	161
-8	-1	0	75	92
-7	-1	0	240	272
-6	-1	0	120	131
-4	-1	0	377	384
-3	-1	0	449	481
-1	-1	0	173	186
1	-1	0	695	690
2	-1	0	262	-255
4	-1	0	681	639
5	-1	0	495	448
8	-1	0	205	191
9	-1	0	114	115
-8	0	0	153	168
-7	0	0	97	109
-5	0	0	297	307
-4	0	0	622	623
-3	0	0	232	242
3	0	0	227	242
4	0	0	616	623
5	0	0	299	302
7	0	0	108	109
8	0	0	190	168
-9	1	0	112	115
-8	1	0	196	191
-6	1	0	58	-41
-5	1	0	491	448
-4	1	0	677	639
-2	1	0	264	-255
-1	1	0	705	690
1	1	0	178	186
3	1	0	454	481
4	1	0	376	384
6	1	0	136	131
7	1	0	303	272
8	1	0	117	92
9	1	0	72	-34
10	1	0	78	39
-9	2	0	147	161
-8	2	0	157	151
-7	2	0	63	-63
-5	2	0	517	485
-4	2	0	440	418
-3	2	0	127	-117
-1	2	0	693	662
1	2	0	67	68
2	2	0	375	413
4	2	0	186	112
5	2	0	163	-156
6	2	0	254	237
7	2	0	348	312
-9	3	0	169	152
-8	3	0	87	79
-6	3	0	107	99
-5	3	0	348	338
-4	3	0	176	174
-2	3	0	419	404
-1	3	0	436	390
0	3	0	64	-55
1	3	0	112	114
2	3	0	540	575
3	3	0	365	388
4	3	0	107	-103
5	3	0	60	-35
6	3	0	307	275
7	3	0	209	191
-7	4	0	68	58
-6	4	0	199	186
-5	4	0	117	102
-3	4	0	207	201
-2	4	0	420	404
-1	4	0	188	178
0	4	0	137	-152
1	4	0	187	179
2	4	0	512	524
3	4	0	134	126
4	4	0	114	-117
5	4	0	146	125
6	4	0	231	203
7	4	0	70	54
-7	5	0	107	109
-6	5	0	185	176
-3	5	0	223	223
-2	5	0	335	316
0	5	0	64	-68
1	5	0	199	196
2	5	0	281	269
5	5	0	169	161
6	5	0	88	93
-7	6	0	90	92
-6	6	0	127	92
-3	6	0	175	186
-2	6	0	136	137
0	6	0	76	77
1	6	0	176	178
4	6	0	113	82
5	6	0	136	123
0	7	0	117	110
1	7	0	130	114
4	7	0	111	85
5	7	0	80	63
-4	-6	1	98	119
-3	-6	1	71	19
-1	-6	1	77	97
0	-6	1	156	183
-5	-5	1	105	157
-4	-5	1	109	131
-1	-5	1	201	214
0	-5	1	154	155
3	-5	1	189	218
4	-5	1	69	76
6	-5	1	66	89
-5	-4	1	164	224
-4	-4	1	93	118
-1	-4	1	289	320
2	-4	1	298	317
3	-4	1	221	263
6	-4	1	138	162
7	-4	1	144	167
-6	-3	1	134	167
-5	-3	1	180	196
-3	-3	1	99	91
-2	-3	1	424	445
-1	-3	1	251	255
0	-3	1	183	-197
1	-3	1	219	231
2	-3	1	577	610
3	-3	1	167	190
4	-3	1	102	-108
5	-3	1	62	72
6	-3	1	220	240
7	-3	1	125	144
-8	-2	1	67	-12
-7	-2	1	85	132
-6	-2	1	263	312
-4	-2	1	143	-152
-3	-2	1	382	413
-1	-2	1	104	115
0	-2	1	244	-237
1	-2	1	340	348
2	-2	1	651	784
3	-2	1	187	198
5	-2	1	223	231
6	-2	1	210	218
9	-2	1	95	112
-10	-1	1	73	67
-7	-1	1	229	285
-6	-1	1	315	352
-5	-1	1	159	-142
-4	-1	1	125	-132
-3	-1	1	731	734
2	-1	1	416	434
3	-1	1	175	168
4	-1	1	261	257
5	-1	1	415	414
6	-1	1	77	63
7	-1	1	83	-81
8	-1	1	149	156
9	-1	1	131	182
-7	0	1	289	368
-6	0	1	171	194
-5	0	1	170	-158
-4	0	1	230	205
-3	0	1	800	757
-2	0	1	394	403
4	0	1	639	594
5	0	1	471	440
8	0	1	182	191
9	0	1	168	175
-8	1	1	128	163
-7	1	1	229	282
-6	1	1	57	42
-5	1	1	124	117
-4	1	1	473	454
-3	1	1	369	372
3	1	1	198	155
4	1	1	784	728
5	1	1	314	273
6	1	1	64	-62
8	1	1	178	173
9	1	1	84	94
-8	2	1	119	156
-7	2	1	98	99
-6	2	1	62	11
-5	2	1	373	373
-4	2	1	589	566
-2	2	1	317	-276
-1	2	1	796	734
1	2	1	158	158
2	2	1	421	-359
3	2	1	362	331
4	2	1	648	580
5	2	1	139	126
7	2	1	181	169
8	2	1	134	123
-8	3	1	102	116
-5	3	1	396	402
-4	3	1	496	499
-3	3	1	161	-134
-2	3	1	182	-152
-1	3	1	840	754
0	3	1	677	620
2	3	1	110	96
3	3	1	396	370
4	3	1	277	250
6	3	1	109	105
7	3	1	239	219
8	3	1	78	50
-9	4	1	83	146
-6	4	1	92	92
-5	4	1	315	321
-4	4	1	218	215
-2	4	1	236	212
-1	4	1	487	456
0	4	1	87	84
2	4	1	421	385
3	4	1	376	359
5	4	1	56	-40
6	4	1	227	200
7	4	1	182	176
-9	5	1	96	108
-6	5	1	126	144
-5	5	1	197	208
-3	5	1	104	80
-2	5	1	331	299
-1	5	1	200	199
0	5	1	62	-39
1	5	1	82	66
2	5	1	400	365
3	5	1	228	209
4	5	1	113	-104
6	5	1	213	194
7	5	1	72	76
-6	6	1	104	121
-5	6	1	88	76
-3	6	1	158	146
-2	6	1	239	234
1	6	1	165	163
2	6	1	256	236
3	6	1	70	36
5	6	1	111	97
6	6	1	141	118
-3	7	1	133	135
-2	7	1	155	155
1	7	1	160	157
2	7	1	123	104
5	7	1	91	89
1	8	1	88	97
4	8	1	80	56
-3	-6	2	92	94
0	-6	2	180	109
1	-6	2	99	95
4	-6	2	95	89
-4	-5	2	145	150
-1	-5	2	109	108
0	-5	2	197	213
1	-5	2	77	75
4	-5	2	181	166
-5	-4	2	153	164
-4	-4	2	211	213
-1	-4	2	280	272
0	-4	2	288	291
3	-4	2	151	151
4	-4	2	186	180
6	-4	2	73	43
7	-4	2	108	97
-5	-3	2	266	266
-4	-3	2	190	182
-3	-3	2	64	-52
-2	-3	2	79	80
-1	-3	2	409	381
0	-3	2	210	202
2	-3	2	225	227
3	-3	2	304	289
6	-3	2	170	162
7	-3	2	159	154
-6	-2	2	152	163
-5	-2	2	304	297
-4	-2	2	107	100
-3	-2	2	60	51
-2	-2	2	316	322
-1	-2	2	392	395
2	-2	2	598	610
3	-2	2	342	345
4	-2	2	169	-158
6	-2	2	288	281
7	-2	2	182	175
-9	-1	2	88	123
-6	-1	2	256	258
-5	-1	2	235	234
-3	-1	2	280	272
-2	-1	2	618	634
2	-1	2	756	751
3	-1	2	209	280
4	-1	2	177	-170
5	-1	2	137	132
6	-1	2	348	332
-10	0	2	81	95
-7	0	2	208	209
-6	0	2	318	299
-5	0	2	58	14
-4	0	2	144	-121
-3	0	2	654	664
2	0	2	650	659
3	0	2	116	111
5	0	2	290	269
6	0	2	251	234
8	0	2	95	69
9	0	2	152	140
-7	1	2	356	378
-6	1	2	249	260
-5	1	2	215	-205
-3	1	2	843	806
-2	1	2	816	764
2	2	2	59	-41
3	2	2	61	58
4	2	2	652	621
5	2	2	348	317
6	2	2	136	-141
8	2	2	226	200
9	2	2	108	112
-8	3	2	138	159
-7	3	2	216	215
-5	3	2	107	101
-4	3	2	478	470
-3	3	2	294	273
-2	3	2	142	-119
-1	3	2	375	328
0	3	2	837	807
1	3	2	299	290
2	3	2	187	-207
3	3	2	202	203
4	3	2	556	518
5	3	2	190	169
6	3	2	76	-78
7	3	2	188	84
8	3	2	158	156
-8	4	2	89	127
-6	4	2	72	68
-5	4	2	293	295
-4	4	2	342	327
-2	4	2	118	-109
-1	4	2	562	523
0	4	2	683	666
1	4	2	88	-74
2	4	2	119	-102
3	4	2	385	365
4	4	2	333	297
7	4	2	143	134
8	4	2	84	83
-6	5	2	78	80
-5	5	2	326	327
-4	5	2	213	198
-3	5	2	128	-108
-1	5	2	478	463
0	5	2	316	306
1	5	2	101	-90
2	5	2	81	83
3	5	2	335	310
4	5	2	115	104
6	5	2	107	108
7	5	2	119	129
8	5	2	73	15
-6	6	2	77	76
-5	6	2	221	220
-4	6	2	102	76
-2	6	2	213	198
-1	6	2	219	219
2	6	2	239	213
3	6	2	190	174
6	6	2	152	137
1	7	2	82	90
2	7	2	229	198
4	7	2	80	-42
6	7	2	116	99
-3	-5	3	127	119
-2	-5	3	71	54
0	-5	3	69	75
1	-5	3	110	110
-4	-4	3	147	148
-3	-4	3	145	139
0	-4	3	190	218
1	-4	3	97	106
4	-4	3	148	169
5	-4	3	89	90
-8	-3	3	81	85
-5	-3	3	100	109
-4	-3	3	240	237
-2	-3	3	84	-89
-1	-3	3	242	257
0	-3	3	324	353
3	-3	3	152	155
4	-3	3	190	215
5	-3	3	63	74
-8	-2	3	74	97
-5	-2	3	304	315
-4	-2	3	228	225
-3	-2	3	143	-139
-1	-2	3	456	474
0	-2	3	404	425
3	-2	3	280	301
4	-2	3	196	195
6	-2	3	95	107
7	-2	3	113	118
-9	-1	3	74	134
-7	-1	3	74	-98
-6	-1	3	127	121
-4	-1	3	130	144
-3	-1	3	92	-88
-2	-1	3	207	224-
0	-1	3	264	268
2	-1	3	259	278
3	-1	3	341	345
6	-1	3	259	265
7	-1	3	150	153
-9	0	3	98	158
-7	0	3	70	-42
-6	0	3	218	221
-5	0	3	358	339
-4	0	3	80	97
-3	0	3	137	127
0	0	3	213	-183
1	0	3	327	336
2	0	3	726	776
3	0	3	214	225
4	0	3	187	-197
5	0	3	68	75
6	0	3	350	352
7	0	3	176	169
8	0	3	75	-41
-7	1	3	97	101
-6	1	3	257	264
-5	1	3	166	170
-4	1	3	97	72
-3	1	3	304	343
-2	1	3	621	681
-1	1	3	71	78
1	1	3	616	679
2	1	3	756	818
4	1	3	139	-122
5	1	3	219	206
6	1	3	306	287
7	1	3	108	96
9	1	3	71	66
-8	2	3	75	40
-7	2	3	230	250
-6	2	3	236	253
-5	2	3	94	-77
-4	2	3	62	59
-3	2	3	639	706
-2	2	3	534	542
-1	2	3	199	-196
1	2	3	608	733
2	2	3	531	522
3	2	3	72	-44
4	2	3	88	73
5	2	3	341	328
6	2	3	157	132
8	2	3	112	98
9	2	3	88	189
-8	3	3	74	114
-7	3	3	300	324
-6	3	3	172	178
-5	3	3	226	-220
-4	3	3	170	144
-2	3	3	330	331
-1	3	3	115	-95
0	3	3	261	254
1	3	3	420	448
2	3	3	253	238
3	3	3	75	68
4	3	3	291	281
5	3	3	285	281
8	3	3	172	163
9	3	3	114	103
-8	4	3	132	160
-7	4	3	238	250
-6	4	3	69	48
-4	4	3	302	286
-3	4	3	404	409
-2	4	3	87	82
-1	4	3	152	142
0	4	3	510	464
1	4	3	215	230
2	4	3	87	-87
3	4	3	182	182
4	4	3	418	413
5	4	3	138	138
6	4	3	106	-89
8	4	3	154	154
9	4	3	84	62
-8	5	3	138	155
-7	5	3	100	110
-5	5	3	172	167
-4	5	3	292	305
-3	5	3	101	94
-1	5	3	269	246
0	5	3	491	484
1	5	3	102	99
2	5	3	149	-158
3	5	3	231	226
4	5	3	341	324
7	5	3	92	88
8	5	3	82	90
-8	6	3	88	92
-5	6	3	190	216
-4	6	3	186	190
-1	6	3	312	314
0	6	3	261	266
3	6	3	239	225
4	6	3	142	147
7	6	3	118	100
-5	7	3	155	172
-4	7	3	78	86
-2	7	3	81	98
-1	7	3	253	271
0	7	3	68	68
2	7	3	128	109
3	7	3	165	157
-5	8	3	82	94
-2	8	3	98	104
-1	8	3	122	119
2	8	3	124	124
3	8	3	83	66
2	9	3	92	88
-3	-5	4	108	71
-2	-5	4	104	71
1	-5	4	75	86
-3	-4	4	158	148
-2	-4	4	91	88
1	-4	4	132	134
-7	-3	4	101	109
-4	-3	4	107	93
-3	-3	4	231	208
0	-3	4	161	157
1	-3	4	131	123
3	-3	4	80	89
4	-3	4	148	160
5	-3	4	74	70
-7	-2	4	79	94
-4	-2	4	237	213
-3	-2	4	169	158
-1	-2	4	142	140
0	-2	4	355	358
1	-2	4	78	70
2	-2	4	94	-92
3	-2	4	163	171
4	-2	4	255	262
6	-2	4	81	-35
7	-2	4	82	41
8	-2	4	106	90
-8	-1	4	108	116
-7	-1	4	77	49
-5	-1	4	242	222
-4	-1	4	300	296
-3	-1	4	72	-62
-1	-1	4	443	425
0	-1	4	428	426
2	-1	4	76	-80
3	-1	4	242	239
4	-1	4	290	287
7	-1	4	106	93
-9	0	4	105	97
-8	0	4	92	83
-6	0	4	98	89
-5	0	4	457	425
-4	0	4	219	204
-3	0	4	281	-260
-2	0	4	163	169
-1	0	4	647	672
0	0	4	366	334
1	0	4	71	-73
2	0	4	84	64
3	0	4	325	334
4	0	4	195	194
7	0	4	133	135
-9	1	4	100	154
-7	1	4	91	-75
-6	1	4	227	227
-5	1	4	478	439
-4	1	4	121	96
-3	1	4	112	-107
-2	1	4	316	385
-1	1	4	549	584
0	1	4	188	188
3	1	4	282	276
5	1	4	92	101
6	1	4	264	268
7	1	4	129	123
-9	2	4	183	159
-6	2	4	310	290
-5	2	4	273	249
-4	2	4	80	81
-2	2	4	477	405
1	2	4	340	388
3	2	4	68	78
4	2	4	209	-207
5	2	4	209	196
6	2	4	331	316
-7	3	4	112	114
-6	3	4	276	255
-5	3	4	110	86
-3	3	4	449	457
-2	3	4	481	505
-1	3	4	187	-110
0	3	4	80	-93
1	3	4	518	596
2	3	4	525	572
4	3	4	97	-101
5	3	4	242	229
6	3	4	253	230
-7	4	4	208	200
-6	4	4	163	156
-4	4	4	94	85
-3	4	4	526	531
-2	4	4	302	333
-1	4	4	201	-193
0	4	4	162	175
1	4	4	494	539
2	4	4	196	205
4	4	4	123	127
5	4	4	233	226
6	4	4	94	74
8	4	4	81	82
9	4	4	81	84
-8	5	4	100	129
-7	5	4	223	228
-6	5	4	84	40
-5	5	4	71	-87
-4	5	4	218	211
-3	5	4	435	443
-2	5	4	119	121
-1	5	4	75	-75
0	5	4	260	264
1	5	4	334	350
4	5	4	236	245
5	5	4	152	149
8	5	4	115	105
-8	6	4	79	120
-7	6	4	161	164
-4	6	4	238	244
-3	6	4	189	198
-1	6	4	136	127
0	6	4	232	248
1	6	4	120	121
2	6	4	57	-33
3	6	4	121	123
4	6	4	238	241
6	6	4	66	-58
-5	7	4	128	109
-4	7	4	201	185
-1	7	4	201	213
0	7	4	208	221
3	7	4	148	153
4	7	4	171	149
-5	8	4	110	113
-4	8	4	110	98
-3	8	4	71	-11
-1	8	4	153	171
0	8	4	123	113
3	8	4	139	120
-1	9	4	115	102
1	-4	5	101	84
2	-4	5	108	107
1	-3	5	168	155
2	-3	5	116	106
-7	-2	5	147	125
-5	-2	5	74	-48
-4	-2	5	77	90
-3	-2	5	242	221
-2	-2	5	113	103
-1	-2	5	78	-47
0	-2	5	103	95
1	-2	5	219	215
2	-2	5	65	55
4	-2	5	144	121
5	-2	5	87	81
-7	-1	5	152	151
-5	-1	5	65	-32
-4	-1	5	189	177
-3	-1	5	257	252
-2	-1	5	89	84
0	-1	5	205	199
1	-1	5	164	152
3	-1	5	140	142
4	-1	5	235	231
6	-1	5	79	-48
8	-1	5	112	100
-8	0	5	153	140
-7	0	5	100	105
-5	0	5	99	82
-4	0	5	309	277
-3	0	5	125	124
-1	0	5	312	307
0	0	5	355	364
3	0	5	271	269
4	0	5	297	301
7	0	5	84	83
8	0	5	107	104
-8	1	5	96	107
-5	1	5	299	274
-4	1	5	312	289
1	1	5	76	-111
3	1	5	328	301
4	1	5	266	255
5	1	5	64	44
7	1	5	102	94
-9	2	5	94	112
-6	2	5	215	179
-5	2	5	446	419
-4	2	5	88	89
-3	2	5	209	-193
-2	2	5	261	258
1	2	5	78	-89
2	2	5	147	161
3	2	5	336	325
4	2	5	71	88
5	2	5	58	50
6	2	5	189	168
7	2	5	94	92
-9	3	5	130	125
-7	3	5	73	-49
-6	3	5	287	279
-5	3	5	407	375
-2	3	5	381	404
-1	3	5	362	402
0	3	5	85	86
1	3	5	64	60
2	3	5	354	342
3	3	5	238	226
5	3	5	100	102
6	3	5	253	239
8	3	5	84	-38
-9	4	5	95	99
-6	4	5	251	239
-5	4	5	209	192
-3	4	5	289	205
-2	4	5	385	355
-1	4	5	84	76
1	4	5	377	376
2	4	5	409	408
4	4	5	75	-81
5	4	5	198	182
6	4	5	236	216
-7	5	5	154	139
-6	5	5	178	146
-4	5	5	78	97
-3	5	5	355	333
-2	5	5	316	289
-1	5	5	132	-116
1	5	5	489	474
2	5	5	298	296
3	5	5	77	-94
5	5	5	201	188
6	5	5	119	128
-7	6	5	174	159
-6	6	5	99	82
-4	6	5	146	138
-3	6	5	336	316
-2	6	5	143	130
-1	6	5	93	-68
0	6	5	161	138
1	6	5	334	304
2	6	5	113	96
4	6	5	108	117
5	6	5	133	141
-7	7	5	115	119
-4	7	5	174	174
-3	7	5	227	219
0	7	5	223	209
1	7	5	136	142
4	7	5	152	147
-4	8	5	166	137
-3	8	5	84	99
-1	8	5	78	75
0	8	5	155	153
4	8	5	113	103
5	8	5	81	12
0	9	5	114	87
-1	-4	6	93	71
1	-3	6	84	67
2	-3	6	89	87
-6	-2	6	117	78
-3	-2	6	121	123
-2	-2	6	128	114
1	-2	6	174	179
2	-2	6	130	135
-6	-1	6	94	77
-4	-1	6	91	80
-3	-1	6	229	218
-2	-1	6	106	86
-1	-1	6	80	-54
1	-1	6	238	236
2	-1	6	125	135
5	-1	6	84	97
-8	0	6	98	74
-7	0	6	172	157
-4	0	6	203	180
-3	0	6	291	264
0	0	6	155	159
1	0	6	219	218
2	0	6	60	54
4	0	6	140	157
5	0	6	82	81
-8	1	6	171	156
-7	1	6	154	141
-4	1	6	265	235
-3	1	6	256	272
-1	1	6	59	69
0	1	6	286	267
1	1	6	81	101
3	1	6	205	203
4	1	6	225	221
8	1	6	119	109
-8	2	6	164	160
-5	2	6	155	131
-4	2	6	197	235
4	2	6	241	226
7	2	6	98	94
8	2	6	97	87
-9	3	6	105	85
-8	3	6	113	96
-6	3	6	69	87
3	3	6	327	318
4	3	6	188	183
6	3	6	63	53
7	3	6	108	90
2	7	6	71	109
3	8	6	70	3
-1	-3	7	99	80
-1	-2	7	106	101
2	-2	7	85	73
-6	-1	7	108	85
-2	-1	7	152	133
1	-1	7	117	109
2	-1	7	125	117
-6	0	7	123	95
-3	0	7	193	184
-2	0	7	98	88
1	0	7	234	234
2	0	7	114	130
3	0	7	71	-49
5	0	7	119	115
6	0	7	97	81
-7	1	7	123	106
-4	1	7	129	137
-1	1	7	81	-87
0	1	7	152	142
1	1	7	278	275
2	1	7	96	108
5	1	7	120	106
-8	2	7	118	109
-7	2	7	176	146
0	2	7	140	195
1	2	7	168	193
3	2	7	79	89
4	2	7	169	157
5	2	7	75	39
-8	3	7	158	167
-7	3	7	100	107
-4	3	7	258	243
4	3	7	213	197
7	3	7	88	83
-8	4	7	132	132
-5	4	7	132	138
-4	4	7	202	201
-1	4	7	217	293
2	4	7	64	72
3	4	7	267	260
4	4	7	158	141
7	4	7	119	92
-6	5	7	102	108
-5	5	7	209	208
-3	5	7	78	-85
-1	5	7	335	389
0	5	7	78	82
1	5	7	90	-101
2	5	7	125	125
3	5	7	229	226
4	5	7	67	76
-6	6	7	171	162
-5	6	7	205	195
-2	6	7	218	216
-1	6	7	260	256
2	6	7	141	148
3	6	7	122	121
5	6	7	81	51
6	6	7	108	90
-6	7	7	161	157
-5	7	7	98	96
-3	7	7	86	92
-2	7	7	224	201
-1	7	7	65	75
1	7	7	90	105
2	7	7	191	160
3	7	7	66	31
5	7	7	75	80
6	7	7	88	86
-6	8	7	99	101
-3	8	7	122	121
-2	8	7	118	127
1	8	7	142	137
2	8	7	94	97
0	9	7	73	64
1	9	7	119	119
-2	-1	8	75	65
-1	-1	8	149	118
2	-1	8	71	42
-2	0	8	144	122
-1	0	8	114	109
2	0	8	86	84
5	0	8	69	63
-6	1	8	155	101
-3	1	8	104	91
-2	1	8	155	152
1	1	8	162	152
2	1	8	101	107
5	1	8	104	91
-6	2	8	105	83
-4	2	8	57	72
-2	2	8	53	66
-1	2	8	57	-71
0	2	8	106	119
1	2	8	252	247
2	2	8	72	78
3	2	8	61	-52
4	2	8	60	31
5	2	8	125	112
6	2	8	75	64
-7	3	8	131	105
-4	3	8	226	189
4	3	8	94	78
5	3	8	108	93
-7	4	8	135	116
-4	4	8	278	227
-3	4	8	182	170
3	4	8	71	81
4	4	8	134	120
-7	5	8	70	58
-5	5	8	78	84
-1	5	8	153	150
0	5	8	182	170
3	5	8	184	177
4	5	8	121	117
5	5	8	58	-21
-4	6	8	114	119
-2	6	8	48	42
-1	6	8	223	199
0	6	8	109	108
1	6	8	46	-45
2	6	8	87	73
3	6	8	183	174
4	6	8	73	61
-6	7	8	78	86
-5	7	8	155	132
-2	7	8	167	145
-1	7	8	210	188
2	7	8	112	110
3	7	8	133	126
-5	8	8	82	102
-2	8	8	150	153
-1	8	8	112	115
2	8	8	107	94
1	9	8	71	75
2	1	9	43	58
3	1	9	53	68
-5	2	9	52	55
-2	2	9	99	139
2	2	9	53	74
5	3	9	69	97
-6	4	9	58	68
4	4	9	44	47
5	4	9	81	93
4	5	9	59	77
5	5	9	57	63
-4	6	9	121	166
0	6	9	100	142
3	6	9	44	70
4	6	9	38	77
-5	7	9	70	86
-4	7	9	90	106
-2	7	9	48	43
-1	7	9	74	110
0	7	9	75	86
3	7	9	74	116
-1	8	9	91	123
2	8	9	41	55
-1	9	9	69	83

electron density than 0.7 e/Å^3. The hydrogen atoms could not be located from this calculation. This is in accordance with the fact that hydrogen contributes on the average only 0.4 % to the intensities.

CRYSTAL DATA

Some relevant crystallographic data are given below.

Crystal system: triclinic, $a = 7.77$ Å, $b = 6.97$ Å, $c = 8.02$ Å, $\alpha = 58.3°$, $\beta = 91.4°$, $\gamma = 92.4°$. Space group $P\bar{1}$ (No. 2). Formula: C$_4$H$_{10}$Cl$_2$Se$_2$Pd. One formula unit per unit cell. Density calc. 2.07 g/cm^3. Absorption coefficient for MoKα $\mu = 68.6$ cm^{-1}.

Final atomic coordinates and temperature factor parameters are given in Tables 2 and 3. Interatomic distances and bond angles are given in Table 4 and observed and calculated structure factors are given in Table 5. The structure is depicted in Fig. 2.

DISCUSSION

The atoms in PdSe$_2$Cl$_2$ are necessarily strictly coplanar if the space group $P\bar{1}$ is correct. This is in accordance with the general trend in the stereochemistry of palladium. The bond length Pd $-$ Cl $= 2.27$ Å differs little from the corresponding bond length 2.29 Å in [Pd((CH$_3$)$_2$SO)$_2$Cl$_2$].[11] We are not aware of other determinations of Pd $-$ Se bond lengths. Palladium-sulfur bond lengths are in general $0.12 - 0.15$ Å shorter than the Pd $-$ Se distance that we report. This is in agreement with the difference between reported covalent radii of S and Se.

The configuration around Se is pyramidal. The two crystallographically independent Se $-$ C bond lengths are equal within the experimental uncertainty and equal the sum of the covalent radii of the two elements. The two C $-$ C bond lengths agree well and are in accordance with the generally expected value for a single bond. The location of the hydrogen atoms were calculated assuming tetrahedral bond angles and a C $-$ H distance of 1.08 Å. The distance from Pd to H was calculated but no indication of a Pd $-$ H bond was found.

The packing of the molecules appears to be governed by Cl $-$ Cl contacts. The centrosymmetric arrangement in the crystal would give a dipole moment of zero if the same structure was maintained on dissolving the compound and if no chemical rearrangements took place. Jensen[1] reports that the dielectric constants of solutions of pure cis or trans compounds change slowly with time but that diethylselenide complexes change more rapidly. Equilibrium seems to be reached in the course of a few weeks. It is therefore unlikely that the finite dipole moments found in freshly made solutions of trans compounds are caused by the presence of appreciable amounts of cis-isomers. We will not attempt an interpretation of the discrepancy between the structures found in the solid state and in solution.

REFERENCES

1. Jensen, K. A. *Z. anorg. allgem. Chem.* **225** (1935) 97.
2. Jensen, K. A. *Z. anorg. allgem. Chem.* **229** (1936) 225.
3. Jensen, K. A. *Om de koordinativt firegyldige metallers stereokemi*, Copenhagen 1937.
4. Arndt, U. W. and Phillips, D. C. *Acta Cryst.* **14** (1961) 807.
5. Grønbæk Hazell, R. *Program G 4*, Department of Inorg. Chem., University of Aarhus.
6. Wells, M. *Acta Cryst.* **13** (1960) 722.
7. Danielsen, J. Program *SYMBAD 1*, Department of Inorg. Chem., University of Aarhus.
8. Cromer, D. T. and Mann, J. T. *Acta Cryst.* **A 24** (1965) 321.
9. Grønbæk Hazell, R. *Program G 3*, Department of Inorg. Chem., University of Aarhus.
10. Stewart, J. *X-Ray 63*, University of Maryland.
11. Bennett, M. S., Cotton, F. A. and Weaver D. L. *Nature* **212** (1966) 286.