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The X-ray Crystal Structure of Diethylammonium Tetracyanopalladate

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The crystal structure of $[(C_2H_5)_2NH_2]_2Pd(CN)_4$ has been determined by inspection of Patterson bidimensional synthesis (*hk*0) and (*h*0*l*) and by refinement of tridimensional intensity data. The space group of the primitive cell is $P\bar{1}$, but a more convenient double cell has been chosen whose space group is $C\bar{1}$, with $a=15{\cdot}79\pm0{\cdot}01$, $b=9{\cdot}10\pm0{\cdot}01$, $c=6{\cdot}35\pm0{\cdot}01$ Å, $\alpha=84°11'\pm1'$, $\beta=92°42'\pm1'$, $\gamma=94°5'\pm1'$. The complex anion is centred on the origin and the distance between two heavy atoms is considerably larger than the corresponding one in the inorganic salts of the $Pd(CN)_4^{2-}$ anion. The latter has the well known square-planar configuration. The four CN ligands are bound to the adjacent cations by H bonds of the N–H···N type, so forming an infinite chain lying in the *b* axis direction. Neighbouring chains in the ($\bar{2}01$) direction form planes whose inclination approximates that of the complex group. The stacking of the planes performs the tridimensional structure. The weak van der Waals bonds between chains and between planes is responsible for the important thermal motion of the atoms.

Introduction

The study of the inorganic salts of $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ complexes in the solid state started with the structural works of Brasseur & de Rassenfosse (1935, 1936, 1937, 1938). Recently, the tridimensional X-ray analysis of $CaPd(CN)_4.5H_2O$ (Fontaine, 1968) and $Rb_2Pd(CN)_4.H_2O$ (Dupont, 1970) confirmed some structural features that are believed characteristic of the complex group present in the crystal lattice.

In the crystals just mentioned, the square-planar ions are always found in columns parallel to the *c*-axis direction. The shortest distance between two neighbouring heavy atoms varies from 3·13 Å in the heptahydrate of Mg^{2+} to 3·72 Å in the monohydrate of Rb^+. Optical properties such as fluorescence emission (Pt compounds only), ultraviolet and visible absorption seem to be related to the heavy-metal spacing (Fontaine, Moreau & Simon, 1968). In order to increase the latter, we have replaced the metallic cation by a large organic one and we have studied the structure and properties of such a compound.

Previous preliminary research (Jérôme-Lerutte, 1967) allows us to choose the diethylammonium salt as a specially demonstrative example.

Crystal data

The cell dimensions and space group of the diethylammonium tetracyanoplatinate have already been published (Jérôme-Lerutte, 1967). The palladate is quite isotypic. It is triclinic; $a=15{\cdot}79\pm0{\cdot}01$, $b=$

$9{\cdot}10 \pm 0{\cdot}01$, $c = 6{\cdot}35 \pm 0{\cdot}01$ Å, $\alpha = 84°11' \pm 1'$, $\beta = 92°42' \pm 1'$, $\gamma = 94°5' \pm 1'$, $D = 1{\cdot}305 \pm 0{\cdot}010$ g.cm^{-3}, $Z = 2$. The cell just described is doubly primitive with space group $C\bar{1}$. It was chosen because it makes the graphical representation of the Patterson and Fourier syntheses easier; also it permits interesting comparisons to be made with the monoclinic cell of the triethylammonium compound whose structure will be published later. No physical test has been performed regarding the symmetry center but the good results obtained with that assumption are sufficient to prove its presence.

Table 1. *Observed and calculated structure factors*

H	FO	FC
K= [illegible] L= 0		
2	721	715
4	274	277
8	506	627
10	514	441
12	472	[illegible]
14	315	266
16	[illegible]	245
18	213	177
20	114	130
K= 1, L= 0		
1	638	660
3	983	1086
5	966	1056
7	304	258
9	488	468
11	354	360
13	358	320
15	327	235
17	235	195
19	122	123
-1	592	657
-5	793	838
-7	200	229
-9	584	563
-11	352	378
-13	344	319
-15	[illegible]	372
-17	198	204
-19	109	133
K= 2, L= 0		
0	1041	1124
2	352	366
4	946	912
6	866	821
8	583	554
10	354	324
12	376	358
14	275	247
16	209	195
18	119	137
-2	219	206
-4	930	1008
-6	803	885
-8	461	504
-10	314	314
-12	401	410
-14	272	276
-16	229	219
-18	162	157
K= 3, L= 0		
1	342	322
3	731	641
5	856	837
7	582	549
9	618	571
11	377	359
13	213	202
15	222	195
17	162	154
19	89	115
-1	394	373
-3	828	823
-5	808	865
-7	583	593
-9	615	602
-11	326	334
-13	276	277
-15	222	226
-17	154	152
-19	122	129
K= 4, L=		
0	955	965
2	526	536
4	368	369
6	502	479
8	573	562
10	432	411
12	327	310
14	205	169
16	175	150
18	101	122
-2	371	361
-4	517	407
-6	558	550
-8	608	616
-10	466	472
-12	342	338
-14	204	158
-16	186	169
-18	169	161
K= 5, L=		
1	571	535
3	519	519
5	454	478
7	350	354
9	384	363
11	302	297
13	209	207
15	208	198
17	122	142
-1	646	636
-3	570	552
-5	431	470
-7	446	430
-9	528	505
-11	274	276
-13	270	239
-15	244	217
-17	176	[illegible]
K= 6, L=		
0	516	496
2	657	675
4	690	[illegible]
6	397	370
8	246	235
10	206	177
12	245	250
14	195	212
16	126	157
-2	331	388
-4	447	453
-6	447	418
-8	226	259
-10	268	219
-12	334	326
-14	253	245
-16	201	193
K= 7, L= 0		
1	446	443
3	396	409
5	318	326
7	220	216
9	232	231
11	192	215
13	156	163
15	120	150
-1	501	497
-3	439	431
-5	322	279
-7	296	261
-9	301	281
-11	228	221
-13	261	249
-15	201	205
K= 8, L= 0		
0	392	417
2	340	344
4	229	256
6	250	259
8	258	253
10	190	182
12	183	159
-2	294	289
-4	318	319
-6	289	263
-8	268	251
-10	274	253
-12	243	220
-14	100	137
K= 9, L= 0		
1	244	232
3	244	240
5	253	253
7	220	222
9	203	203
11	135	156
-1	278	268
-3	254	246
-5	258	233
-7	322	296
-9	295	268
-11	158	154
-13	104	132
K= 10, L= 0		
0	148	155
2	161	176
4	210	210
6	214	219
8	149	187
-2	169	180
-4	302	285
-6	270	258
-8	181	184
-10	153	161
K= 11, L= 0		
1	127	156
3	157	165
5	98	161
1	168	181
-3	138	188
-5	162	178
-7	132	176
K= 0, L= 1		
0	445	519
2	1031	1083
4	291	279
6	638	636
8	506	477
10	661	618
12	377	329
14	370	346
16	274	263
18	179	167
-4	1034	1155
-6	430	468
-8	411	362
-10	426	399
-12	265	245
-14	348	321
-16	219	198
-18	179	165
K= 1, L= 1		
1	1032	1125
3	[illegible]	[illegible]
5	[illegible]	495
7	739	810
9	434	376
11	682	657
13	352	372
15	255	261
17	195	181
-1	1089	1207
-5	701	683
-7	532	442
-9	420	343
-11	405	389
-13	337	320
-15	214	204
-17	184	196
-19	149	155
K= -1, L= 1		
1	1210	1024
3	121	127
5	593	594
7	781	817
9	398	389
11	469	449
13	372	373
15	293	279
17	197	196
19	134	152
-1	1216	1190
-3	983	1006
-5	590	720
-7	525	524
-9	339	381
-11	256	323
-13	326	308
-15	190	205
-17	158	167
-19	129	144
K= 2, L= 1		
0	272	247
2	1432	1534
4	883	944
6	576	548
8	265	231
10	566	551
12	385	350
14	275	266
16	197	199
-2	484	501
-4	549	503
-6	669	731
-8	698	717
-10	434	424
-12	219	222
-14	305	300
-16	193	194
-18	147	150
K= -2, L= 1		
0	334	332
0	360	333
4	944	948
6	461	436
8	289	298
10	610	588
12	373	350
14	311	298
16	198	205
18	159	168
-2	149	143
-4	491	523
-6	677	702
-8	656	659
-10	454	453
-12	172	183
-14	261	268
-16	183	169
-18	131	134
K= 3, L= 1		
1	948	933
3	736	732
5	702	688
7	739	776
9	395	389
11	927	913
13	236	234
15	200	198
-1	316	271
-3	410	414
-5	633	627
-7	666	674
-9	458	455
-11	407	410
-13	294	292
-15	183	188
-17	154	157
-19	85	122
K= -3, L=		
1	711	712
3	520	497
5	849	891
7	773	760
9	375	349
11	393	360
13	263	264
15	205	202
17	195	192
19	154	182
-1	575	605
-3	456	469
-5	486	491
-7	694	677
-9	434	444
-11	414	397
-13	312	298
-15	167	156
-17	96	129
K= 4, L= 1		
0	393	370
2	465	464
8	504	497
10	386	376
12	171	186
-2	879	949
-4	500	483
-6	293	310
-8	495	489
-10	500	480
-12	352	324
-14	270	262
-16	123	134
-18	94	116
K= -4, L= 1		
0	389	403
2	669	652
4	542	538
6	687	708
8	573	581
10	421	398
12	135	140
14	265	244
16	238	225
18	173	174
-4	548	529
-6	320	317
-8	384	387
-10	441	439
-12	231	237
-14	216	218
-16	127	134
K= 5, L= 1		
1	645	633
3	481	467
-1	481	459
-3	524	534
-5	551	527
-7	450	425
-9	333	328
-11	353	351
-13	248	245
-15	165	167
-17	160	153
K= -5, L= 1		
1	539	512
3	374	378
5	585	575
7	498	489
9	318	300
11	371	346
13	286	270
15	216	208
17	173	168
-1	573	562
-3	473	481
-5	461	478
-7	397	378
-9	259	260
-11	238	227
-13	228	225
-15	156	164
K= 6, L= 1		
0	471	446
2	570	536
-2	617	606
-4	438	411
-6	420	394
-8	403	380
-10	277	249
-12	183	178
-14	242	225
-16	159	172
K= 6, L= 1		
0	448	436
2	636	610
4	359	346
6	267	234
8	311	282
10	417	394
12	327	301
14	291	265
16	152	154
-2	450	431
-4	454	431
-6	375	361
-8	283	279
-10	248	235
-12	132	133
-14	150	163
K= 7, L= 1		
1	519	502
-1	394	372
-3	433	403
-5	508	467
-7	375	335
-9	202	187
-11	215	199
-13	201	189
-15	183	178
K= -7, L= 1		
1	427	405
3	325	305
5	347	296
7	262	251
9	286	258
11	397	338
13	262	241
15	153	160
-1	464	439
-3	381	365
-5	349	344
-7	299	283
-9	185	181
-11	162	153
-13	159	155
K= 8, L= 1		
0	389	352
-2	539	486
-4	320	295
-6	244	217
-8	274	243
-10	261	230
-12	229	191
-14	172	172
K= -8, L= 1		
0	283	276
2	301	271
4	263	265
6	379	326
8	353	312
10	242	217
12	146	145
14	174	189
-2	385	364
-4	343	316
-6	201	205
-8	177	178
-10	221	208
-12	143	140
K= 9, L= 1		
-1	236	217
-3	284	246
-5	293	265
-7	246	225
-9	244	220
-11	232	217
-13	125	142
K= -9, L= 1		
1	280	247
3	305	275
5	353	315
7	278	246
9	192	171
11	190	168
-1	255	234
-3	187	179
-5	202	194
-7	237	219
-9	180	178
-11	104	137
K= 10, L= 1		
-4	172	162
-6	253	226
-8	272	238
-10	175	175
K= -10, L= 1		
0	175	179
2	309	271
4	265	244
6	223	204
8	187	182
10	120	156
-2	139	144
-4	179	164
-6	165	165
-8	118	149
K= -11, L= 1		
1	167	175
3	164	176
5	146	176
K= -11, L= 1		
-1	165	174
-3	107	139
K= 0, L= 2		
0	238	259
2	301	278
6	756	761
8	669	621
10	303	275
12	530	492
14	367	327
16	219	210
18	117	132
-2	776	681
-4	1179	1256
-6	845	826
-8	404	357
-10	183	178
-12	378	344
-14	190	169
-16	187	172
-18	132	138
K= 1, L= 2		
1	439	392
3	751	737
5	573	526
7	482	450
9	635	595
11	511	462
13	330	323
15	226	231
17	178	197
-3	991	1007
-5	572	542
-9	405	399
-11	258	243
-13	251	242
-15	213	200
-17	161	159
-19	81	103
K= -1, L= 2		
1	623	689
3	778	761
5	414	423
7	456	458
9	649	621
11	460	446
13	314	320
15	242	252
17	187	198
19	92	124
-1	743	816
-3	789	773
-5	292	294
-7	586	610
-9	567	503
-11	258	256
-13	187	200
-15	176	177
-17	141	158
-19	66	94
K= 2, L= 2		
0	1123	1176
2	850	834
4	484	457
6	396	413
8	669	655
10	367	358
12	373	368
14	234	229
16	197	215
-2	535	534
-4	373	394
-6	502	506
-8	526	479
-10	386	371
-12	367	357
-14	167	158
-16	186	176
-18	133	137
K= -2, L= 2		
0	973	941
0	823	944
2	696	730
4	552	556
6	503	473
8	567	602
10	362	349
12	390	404
14	230	221
16	206	220
18	173	195
-2	518	497
-4	480	466
-6	422	427
-8	434	438
-10	298	287
-12	373	373
-14	172	175
-16	142	141
-18	86	112
K= 3, L= 2		
1	573	553
3	887	915
5	662	661
7	404	414
9	391	382
11	289	286
13	247	246
15	226	239
-1	754	765
-3	571	542
-5	279	289
-9	440	458
-11	325	325
-13	280	278
-15	192	201
-17	123	139
-19	60	90
K= -3, L= 2		
1	731	727
3	857	892
5	504	496
7	451	439
9	448	444

Table 1 (*cont.*)

H	FO	FC
11	280	269
13	236	234
15	258	266
17	228	236
-1	612	625
-3	547	524
-5	219	228
-7	342	338
-9	411	409
-11	304	298
-13	225	239
-15	160	166
-17	107	125
K= 4, L= 2		
0	612	623
2	595	615
6	553	574
8	433	455
10	139	155
12	264	275
-2	333	322
-4	463	462
-6	469	479
-8	359	363
-10	320	318
-12	328	338
-14	197	193
-16	173	171
-18	88	111
K= -4, L= 2		
0	410	401
2	484	469
4	777	814
6	642	661
8	330	321
10	132	136
12	347	340
14	272	266
16	203	223
18	121	167
-2	381	377
-4	522	520
-6	437	438
-8	295	295
-10	164	178
-12	284	287
-14	182	183
-16	112	128
K= 5, L= 2		
1	262	269
3	546	573
-1	522	510
-3	593	597
-5	466	463
-7	361	355
-9	277	286
-11	262	258
-13	265	255
-15	173	177
-17	94	114
K= -5, L= 2		
1	447	450
3	512	515
5	346	349
7	398	372
9	413	411
11	285	293
13	251	247
15	221	213
17	124	156
-1	438	433
-3	477	465
-5	335	326
-7	315	304
-9	308	[illegible]
-11	200	199
-13	137	152
-15	121	125
K= 6, L= 2		
0	612	592
2	434	433
-2	373	370
-4	389	374
-6	419	401
-8	367	360
-10	294	274
-12	191	200
-14	102	123
-16	132	147
K= -6, L= 2		
0	491	437
2	294	290
4	263	236
6	320	317
8	419	405
10	378	359
12	234	313
14	145	147
16	117	135
-2	386	377
-4	325	330
-6	341	344
-8	291	296
-10	156	159
-12	148	157
-14	96	113
K= 7, L= 2		
1	263	272
-1	471	459
-3	436	439
-5	363	344
-7	340	331
-9	248	251
-11	167	165
-13	161	157
-15	121	139
K= -7, L= 2		
1	280	263
3	305	295
5	263	259
7	334	317
9	370	350
11	243	242
13	192	195
15	135	173
-1	294	290
-3	390	390
-5	307	304
-7	219	218
-9	197	203
-11	143	150
-13	133	114
K= 8, L= 2		
0	298	291
-2	289	289
-4	393	364
-6	315	302
-8	215	210
-10	187	187
-12	163	147
-14	101	128
K= -8, L= 2		
0	271	271
2	239	237
4	341	315
6	322	360
8	225	200
10	174	171
12	207	224
-2	245	236
-4	228	237
-6	233	232
-8	193	193
-10	114	127
-12	103	129
K= 9, L= 2		
-1	201	201
-3	257	252
-5	210	210
-7	221	205
-9	182	182
-11	154	165
-13	135	160
K= -9, L= 2		
1	267	257
3	327	299
5	252	229
7	198	170
9	160	169
11	110	151
-1	192	190
-3	197	200
-5	162	166
-7	127	133
-9	127	145
K= 10, L= 2		
-4	172	169
-6	158	160
-8	160	172
-10	158	182
K= -10, L= 2		
0	250	242
2	208	238
4	192	189
6	147	174
8	133	141
-2	140	173
-4	91	[illegible]
-6	[illegible]	119
K= [illegible], L= 3		
0	230	[illegible]
2	527	554
4	747	714
6	495	493
8	[illegible]	[illegible]
10	605	[illegible]
12	[illegible]	335
14	255	247
16	151	156
18	125	156
-2	544	571
-4	452	475
-6	[illegible]	561
-8	[illegible]	482
-10	370	[illegible]
-12	159	144
-14	160	163
-16	153	137
-18	93	91
K= 1, L= 3		
1	546	570
3	494	528
5	500	525
7	583	575
9	519	459
11	397	355
-1	397	433
-3	362	386
-5	643	711
-7	479	493
-9	297	298
-11	286	301
-13	159	166
-15	148	147
-17	108	116
K= -1, L= 3		
1	559	591
3	459	470
5	491	527
7	560	572
9	451	429
11	381	353
13	330	313
15	221	214
17	134	160
-1	465	505
-3	390	364
-5	623	600
-7	453	429
-9	303	247
-11	373	311
-13	213	186
K= 2, L= 3		
0	540	545
2	409	407
4	498	506
6	564	544
8	440	441
10	492	434
12	268	228
14	291	259
-2	741	784
-4	411	474
-6	417	429
-8	355	313
-10	330	313
-12	200	209
-14	248	210
-16	145	140
K= -2, L= 3		
0	535	552
2	367	385
4	431	443
6	521	521
8	466	459
10	425	428
12	210	195
14	295	281
-2	856	929
-4	365	395
K= 3, L= 3		
1	769	746
3	446	436
5	449	440
7	477	452
9	338	360
11	252	249
-1	744	760
-3	508	493
-5	358	349
-7	206	216
-9	282	237
-11	361	345
-13	198	195
-15	159	160
K= -3, L= 3		
1	473	601
3	560	589
5	435	466
7	328	335
9	251	237
11	321	301
13	349	330
15	263	255
17	165	191
-1	473	471
-3	209	223
-5	[illegible]	[illegible]
-7	344	345
-9	170	159
-11	247	227
-13	[illegible]	189
K= [illegible], L= 4		
[illegible]	[illegible]	[illegible]
2	515	522
4	394	393
6	419	425
8	508	496
10	325	332
12	296	269
14	159	169
16	152	167
-2	201	226
-4	347	[illegible]
-6	341	341
-8	326	299
-10	312	270
-12	218	197
-16	124	89
K= 1, L= 4		
1	411	426
3	466	492
5	480	494
7	395	404
9	426	395
11	367	312
-1	397	422
-3	268	296
-5	277	284
-7	383	275
-9	353	368
-11	171	175
-13	143	150
-15	136	119
K= -1, L= 4		
1	301	297
3	447	452
5	522	536
7	406	387
9	384	357
11	309	296
13	232	216
15	209	205
17	145	183
-1	413	420
-3	463	455
-5	354	321
-7	270	250
-9	323	283
-11	203	182
-13	183	158
K= 2, L= 4		
0	326	383
2	370	388
4	440	449
6	473	471
8	412	387
10	240	229
12	328	291
14	282	269
-2	339	361
-4	553	579
-6	338	334
-8	260	213
-10	239	218
-12	223	199
K= -2, L= 4		
0	464	481
2	374	397
4	377	395
6	406	400
8	362	336
10	199	218
12	348	321
14	286	275
16	173	194
-2	275	304
-4	435	411
K= 3, L= 4		
1	421	426
3	412	419
5	393	382
7	265	263
9	321	292
11	379	338
-1	511	490
-3	424	436
-5	367	328
-7	368	377
-9	213	248
-13	142	167
-15	127	136
-17	72	92
K= -3, L= 4		
1	355	350
3	[illegible]	386
5	327	319
7	231	221
9	326	321
11	332	327
11	[illegible]	[illegible]
13	261	260
15	[illegible]	[illegible]
-1	449	434
-3	[illegible]	[illegible]
-5	[illegible]	290
-7	[illegible]	192
-9	237	217
-11	130	138
K= [illegible], L= [illegible]		
[illegible]	329	[illegible]
2	326	326
4	366	376
6	383	390
8	[illegible]	[illegible]
10	273	253
12	149	152
14	169	175
-2	264	275
-4	176	202
-6	188	170
-8	242	225
-10	209	180
-12	167	147
K= 1, L= 5		
1	372	395
3	384	374
5	333	339
7	368	361
9	309	267
11	221	190
-1	256	253
-3	244	269
-5	258	271
-7	229	216
-9	174	178
-11	190	175
-13	130	129
K= -1, L= 5		
1	377	376
3	365	361
5	319	317
7	332	322
9	268	248
11	237	221
13	231	224
15	141	179
-1	244	239
-3	274	261
-5	298	281
-7	244	215
-9	165	155
-13	129	113
K= 2, L= 5		
0	301	320
2	331	338
4	455	369
6	330	318
8	270	230
10	313	292
12	235	255
14	189	195
-2	358	350
-4	197	208
-6	226	220
-8	274	260
K= -2, L= 5		
0	254	248
2	312	320
4	327	334
6	268	254
8	231	214
10	298	313
12	258	258
14	189	194
-2	317	309
-4	266	259
K= 3, L= 5		
1	314	318
3	323	328
5	233	250
7	282	283
9	312	295
11	288	264
-1	203	217
-3	319	326
-5	354	364
-7	246	260
-9	121	130
-11	147	131
-13	132	112
-15	77	89
K= -3, L= 5		
1	306	307
3	155	176
5	183	198
7	322	315
9	293	285
11	245	247
13	206	219
-1	317	308
-3	295	268
-5	247	232
-7	171	183
-9	142	144
-11	111	118
K= [illegible], L= 6		
0	278	257
2	285	290
4	273	264
6	229	231
8	224	213
10	166	165
12	141	179
-2	195	182
-4	265	194
-6	193	177
-8	148	128
K= 1, L= 6		
1	194	217
3	238	262
5	206	203
7	211	213
9	195	175
-1	262	283
-3	236	238
-5	146	153
-9	156	119
-11	111	117
-13	86	99
K= -1, L= 5		
1	230	222
3	249	252
5	252	243
7	203	192
9	211	208
11	206	209
-1	263	250
-3	220	203
-5	176	155
-7	180	151
K= 2, L= 6		
0	300	257
2	275	296
4	224	231
8	280	254
10	200	213
12	177	182
K= -2, L= 5		
0	224	221
2	237	221
6	194	213
8	274	263
10	221	211
K= 3, L= 6		
1	179	189
3	194	205
5	249	251
7	221	249
9	244	236
-1	230	243
-3	196	213
-5	185	177
-7	162	171
-9	147	136
-11	106	108
K= -3, L= 5		
1	155	141
3	169	189
5	230	232
7	[illegible]	[illegible]
9	230	219
11	165	189
-1	173	184
-3	197	190
-5	166	157
-7	152	149
-9	108	110
K= 0, L= 7		
0	140	169
2	181	172
4	182	185
6	151	155
-2	183	157
K= 1, L= 7		
1	199	203
3	175	186
5	160	150
7	163	155
-1	205	168
-3	137	149
-5	122	123
K= -1, L= 7		
1	195	192
3	163	154
5	140	144
7	176	178
-1	169	157
-3	153	136
-5	136	116
K= -2, L= 7		
4	179	175
6	182	185
K= 2, L= 7		
1	155	173
3	148	177
5	160	171
7	196	192
-1	171	144
-3	132	135
-5	125	118
-7	106	133
K= -3, L= 7		
1	138	140
3	147	156
5	145	163
-1	86	103
-3	92	106
-5	120	114

Experimental

Intensity data were recorded photographically with Cu $K\alpha$ radiation by the multiple-film technique using an integrating Weissenberg camera. The intensities corresponding to the reciprocal lattice planes ($hk0$), ($hk1$), ($hk2$), ($h0l$), ($h1l$), ($h2l$) and ($h3l$) were investigated and measured with a Unicam microdensitometer. Eighty-seven unknown parameters, including 60 anisotropic thermal motion factors, were determined from the intensity data. The proportion of accidentally extinguished intensities was quite low because the heavy metal being at the cell origin influenced all reflexions equally. They were not included in the refinement as they could not change the structure results. A few experimental data close to the reciprocal lattice origin were also discarded since they were affected by secondary extinctions. The intensities of the 1169 remaining reflexions were corrected for the Lorentz and polarization effects as well as for absorption. An IBM 7090 computer program written by Dideberg (1966) was used for the latter correction.

Solution and refinement of the structure

A first attempt to locate C and N atoms was performed by means of (*hk*0) and (*h*0*l*) Patterson maps (Figs. 1 & 2). The heavy atom is necessarily situated on the symmetry centre and CN ligands appear in the peaks nearest the heavy atom. The diethylammonium ion is more difficult to locate but its location is obtained by means of stereochemical considerations. After a few trials, the Pd, C and N positional parameters and isotropic temperature factors were included in a refinement cycle. The corresponding *R* factor (10·9%) doubtless shows the accuracy of the atoms ordering in the unit cell. The whole set of measured intensities was refined by the full-matrix least-squares method with anisotropic thermal motion factors for the atoms including hydrogen atoms. After a few cycles, an ultimate *R* factor of 5·5% was obtained and convergence was reached for Pd, C and N parameters. The least-square calculation was performed on an IBM 7040 computer using program *ORFLS* (Busing, Martin & Levy, 1962). The observed and calculated structure factors are listed in Table 1. Atomic diffusion factors are taken from tables published by Cromer & Waber (1965). Coordinates and temperature factors of non-hydrogen atoms are described in Table 2.

Determination of the hydrogen atomic positions

In the first step of the work, H-atom contributions were neglected but the estimated C–C and C–N distances were systematically longer than the average literature values. H atoms were then introduced in hypothetical positions according to the following principles: C and N^+ atom hybridization is tetrahedral, C–H distance is 1·09 Å, N–H(1) is 1·01 Å. Thus 6 of the 12 H atoms

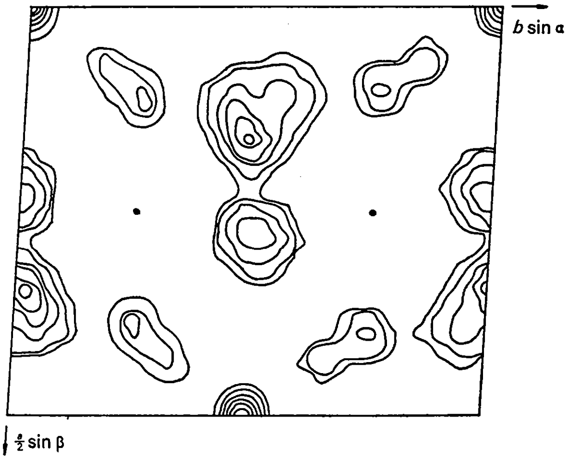

Fig. 1. Patterson map (001).

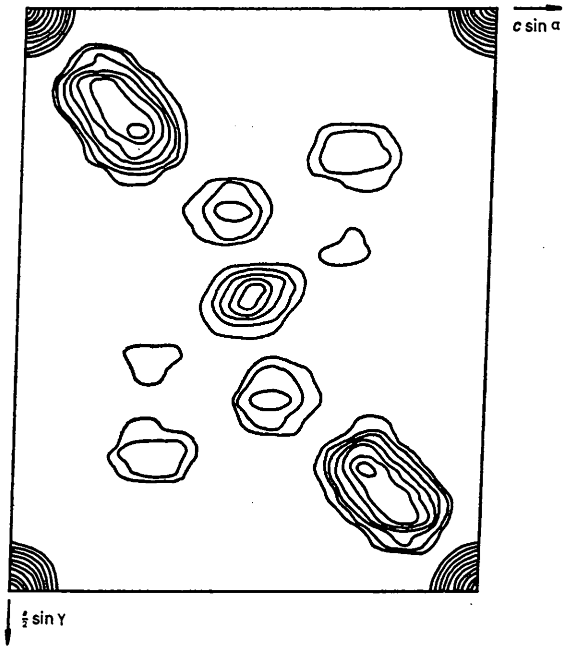

Fig. 2. Patterson map (010).

Table 2. *Coordinates and anisotropic temperature coefficients of non-hydrogen atoms* (*e.s.d.'s in parentheses*)

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

	$\frac{x}{a}(10^4\,\sigma x)$	$\frac{y}{b}(10^4\,\sigma y)$	$\frac{z}{c}(10^4\,\sigma z)$	$10^4\beta_{11}(\sigma_{11})$	$10^4\beta_{22}(\sigma_{22})$	$10^4\beta_{33}(\sigma_{33})$	$10^4\beta_{12}(\sigma_{12})$	$10^4\beta_{13}(\sigma_{13})$	$10^4\beta_{23}(\sigma_{23})$
Pd	0	0	0	30·3 (0·3)	69·9 (1·2)	208 (2.9)	4.6 (0.4)	−25.4 (0.6)	−17.1 (1.4)
C(1)	0·0687 (7)	0·1513 (13)	0·1424 (18)	54 (4)	128 (14)	416 (32)	21 (7)	−46 (10)	28 (22)
C(2)	0·0656 (6)	0·8438 (12)	0·1641 (16)	50 (4)	105 (12)	349 (27)	−6 (6)	−29 (8)	−59 (20)
C(3)	0·1078 (17)	0·5519 (26)	0·7803 (26)	164 (21)	350 (44)	460 (50)	77 (25)	54 (25)	−20 (43)
C(4)	0·1140 (12)	0·4333 (19)	0·6562 (24)	109 (10)	199 (25)	474 (45)	−3 (13)	62 (18)	−24 (34)
C(5)	0·2548 (8)	0·4982 (20)	0·4939 (27)	48 (5)	274 (30)	740 (74)	7 (10)	−54 (16)	6 (42)
C(6)	0·2969 (11)	0·5207 (27)	0·2813 (35)	69 (8)	398 (50)	852 (88)	−9 (16)	79 (23)	−4 (54)
N(1)	0·1107 (8)	0·2432 (13)	0·2202 (21)	82 (6)	150 (17)	687 (47)	2 (8)	−125 (14)	−87 (25)
N(2)	0·1030 (7)	0·7523 (11)	0·2574 (16)	72 (5)	143 (14)	464 (31)	35 (7)	−59 (10)	35 (20)
N(3)	0·1619 (5)	0·4784 (10)	0·4597 (13)	51 (3)	135 (12)	343 (22)	16 (5)	−23 (7)	−4 (16)

were unambiguously located, the 6 others occupying vertexes of tetrahedra whose orientation is not known. Their positions were chosen by accounting for possible sterical hindrances. Later on, attempts were made to introduce the positional parameters of H atoms as variable quantities. The temperature factors were equal to the last isotropic factor of the C or N atom to which the H atom is attached. Positional errors were important and convergence was not reached for all atoms. But the hypothesis of an improvement of the proposed model was acceptable according to the Hamilton (1965) significance tests.

Hydrogen coordinates and their temperature factors are listed in Table 3.

Table 3. *Hydrogen coordinates and temperature-factor coefficients*

$$T=\exp\left(-B\,\frac{\sin^2\theta}{\lambda^2}\right).$$

	$\frac{x}{a}$ ($10^3\,\sigma x$)	$\frac{y}{b}$ ($10^4\,\sigma y$)	$\frac{z}{c}$ ($10^4\,\sigma z$)	T
H(1)	0·142 (9)	0·379 (16)	0·373 (19)	5·14
H(2)	0·134 (9)	0·577 (16)	0·421 (19)	5·14
H(3)	0·146 (12)	0·320 (22)	0·758 (27)	9·13
H(4)	0·047 (12)	0·386 (20)	0·598 (25)	9·13
H(5)	0·242 (11)	0·630 (19)	0·626 (23)	7·31
H(6)	0·272 (11)	0·399 (19)	0·643 (23)	7·31
H(7)	0·108 (14)	0·660 (25)	0·656 (31)	10·84
H(8)	0·182 (15)	0·610 (26)	0·884 (31)	10·84
H(9)	0·109 (15)	0·508 (24)	0·875 (29)	10·84
H(10)	0·356 (13)	0·582 (24)	0·260 (29)	9·86
H(11)	0·262 (13)	0·636 (23)	0·166 (28)	9·86
H(12)	0·320 (13)	0·403 (24)	0·168 (29)	9·86

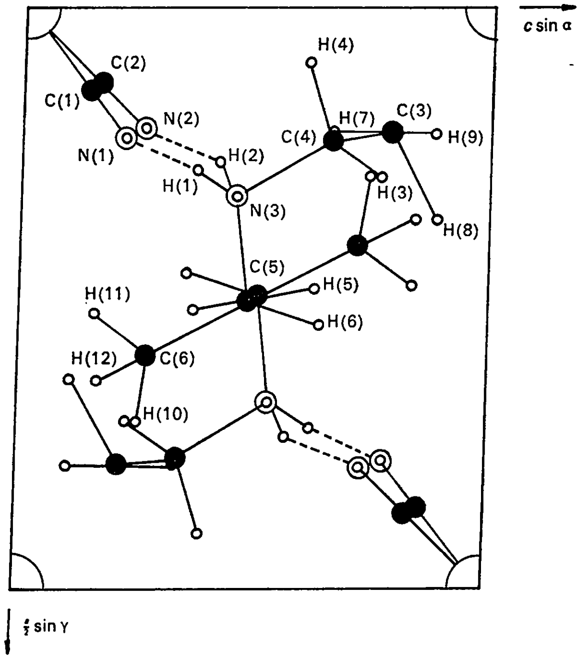

Fig. 3. Projection of the structure on the (001) plane.

Description of the structure

Bond lengths, bond angles and their associated standard deviations are listed in Tables 4 and 5. Projections of the structure on the (001) and (010) planes are shown in Figs. 3 and 4 respectively.

Table 4. *Bond length (e.s.d.'s in parentheses)*

Pd—C(1)	1·970 (15) Å
Pd—C(2)	2·001 (12)
C(1)–N(1)	1·173 (16)
C(2)–N(2)	1·156 (13)
C(3)–C(4)	1·419 (26)
C(5)–C(6)	1·530 (25)
C(4)–N(3)	1·504 (17)
C(5)–N(3)	1·478 (15)
C(3)–H(7)	1·2 (2)
C(3)–H(8)	1·4 (2)
C(3)–H(9)	0·7 (2)
C(4)–H(3)	1·2 (2)
C(4)–H(4)	1·2 (2)
C(5)–H(5)	1·6 (2)
C(5)–H(6)	1·3 (2)
C(6)–H(10)	1·1 (2)
C(6)–H(11)	1·4 (2)
C(6)–H(12)	1·4 (2)
N(3)–H(1)	1·13 (15)
N(3)–H(2)	1·03 (14)

Table 5. *Bond angles (e.s.d.'s in parentheses)*

C(1)—Pd—C(2′)	89·4 (0·4)°
N(1)—Pd—N(2′)	90·1 (0·4)
Pd——C(1)–N(1)	177·5 (1·2)
Pd——C(2)–N(2)	179·1 (0·9)
C(3)—C(4)–N(3)	112·6 (1·5)
C(4)—N(3)–C(3)	114·4 (1·1)
N(3)—C(3)–C(6)	109·3 (1·3)
H(1)—N(3)–H(2)	125 (10)
H(3)—C(4)–H(4)	107 (12)
H(5)—C(5)–H(6)	92 (8)
H(7)—C(3)–H(8)	94 (12)
H(8)—C(3)–H(9)	97 (23)
H(7)—C(3)–H(9)	145 (26)
H(10)-C(6)–H(11)	85 (14)
H(11)-C(6)–H(12)	121 (11)
H(10)-C(6)–H(12)	102 (15)

The complex group has the well known square-planar configuration. Pd–C and C–N distances are in accordance with the values listed by Fontaine (1968) and Dupont (1970). The $Pd(CN)_4^{2-}$ ion is only slightly distorted from the theoretical D_{4h} symmetry. The mean plane calculated by the program of Pippy & Ahmed (1966) has the following equation:

$$0{\cdot}686x-0{\cdot}015y-0{\cdot}727z=0\,.$$

The planarity is unquestionable since no out-of-plane distortion exceeds 3σ. The group is approximately situated in the ($\bar{2}$01) plane. The diethylammonium cation lies approximately in a plane parallel to (010) and distant $\frac{1}{2}b$ from the origin. C–N sp^3 distances agree with the average experimental value and with the theoretical one: 1·47 Å. The situation is not so clear for C–C distances: one value agrees fairly well with the theoretical 1·55 Å value but the other is wrong: the discrepancy is beyond the 3σ limit. Such a contraction has no chemical explanation since the measured length should be about an sp^2 C–C distance. Neither is the presence of systematic errors an explanation as no reflexion is specially affected by the C(3) atom displacement in its assumed position. A unique least-squares refinement brings it back in its place. Since thermal motion amplifies itself considerably at the cationic chain bottoms, the mean position could possibly be erroneous but only a low-temperature study should eliminate that kind of error.

H bonds

Two H atoms are attached to the N(3) atom and point towards the N atoms of the CN ligands. The measured distances and angles are listed in Table 6.

Table 6. *Distances and angles in the H-bond system*

N(1)···H(1)	1·69 (0·15) Å
N(1)···N(3)	2·82 (0·02)
N(2)···H(2)	1·90 (0·14)
N(2)···N(3)	2·89 (0·02)
N(1)···N(3)···N(2)	110·5 (0·4)
N(1)···H(1)···N(3)	174 (10)
N(2)···H(2)···N(3)	159 (10)
C(1) ≡ N(1)···N(3)	161·8 (1·2)
C(2) ≡ N(2)···N(3)	166·2 (0·9)

The N(1)···N(3) and N(2)···N(3) distances confirm the presence of two H bonds of the N–H···N type. According to Pimentel & McClellan (1960), the mean distance of such bonds is 3·10 Å. Therefore, here they seem stronger than the average one. The accuracy of H positions is not sufficient to state the linearity of these bonds. In the large error limits, they do not seem highly bent. The ratio of H donor (NH bond) to H acceptor (CN ligand) is unity. So all N atoms in the structure take part in H-bond formation and contribute to the building of infinite chains lying in the b-axis direction (Fig. 5).

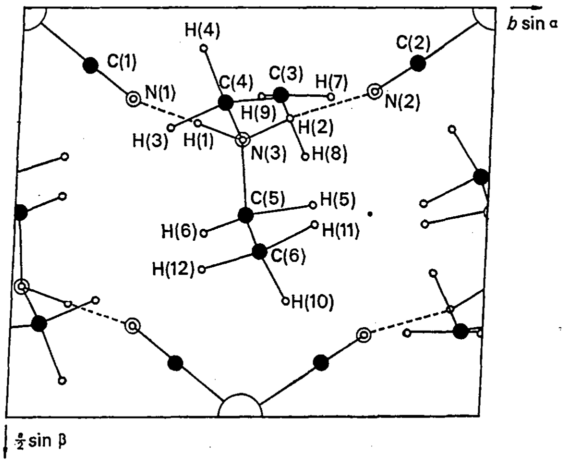

Fig. 4. Projection of the structure on the (010) plane.

Packing

The chains parallel to the b axis lie side by side in the ($\bar{2}01$) plane with a displacement of $\frac{1}{2}b$ between consecutive chains, as shown in Fig. 5. Fig. 6 shows the projection of the chains on the ($\bar{2}01$) plane, with their

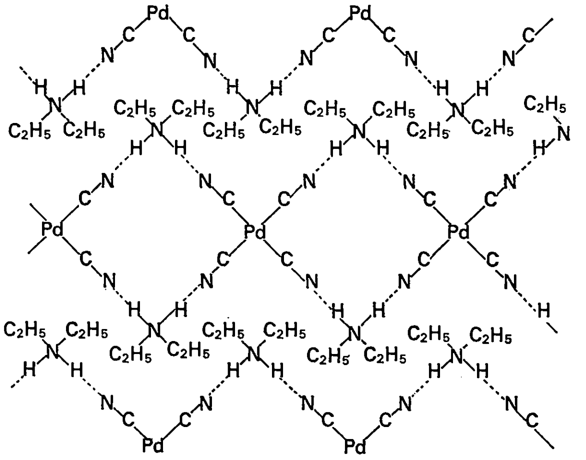

Fig. 5. Schematic representation of the chain formation along the b axis direction in the ($\bar{2}01$) plane.

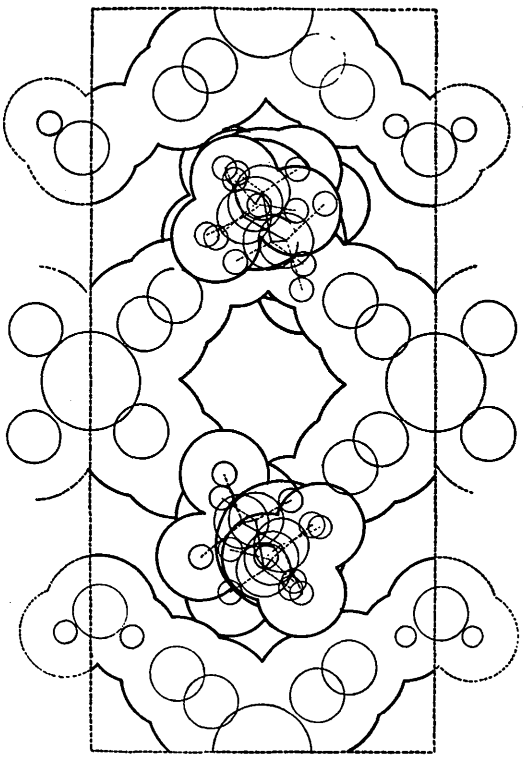

Fig. 6. Projection of the chains on the ($\bar{2}01$) plane.

insistent sterical occupation. The outer circles in thick full line represent van der Waals spheres, whereas the inner circles in thin full line indicate the covalence spheres. Four contact distances between chains have been calculated, *i.e.* distances approximately equal to the sum of the van der Waals radii. Fig. 7 shows the stacking of ($\bar{2}01$) planes through a projection of a (010) section between about $x=-0{\cdot}25$ and $x=0{\cdot}25$. The complex groups are centered at the four corners of the cell. Between them, two cationic unities lie in the normal direction to the ($\bar{2}01$) plane. One ethyl group touches the $Pd(CN)_4^{2-}$ ion; two contact distances have been found at this place. Another plane–plane contact probably exists at the other end of the diethylammonium group between two H atoms. Table 7 lists the contact distances between non-bonded atoms.

Table 7. *Contact distances between non-bonded atoms (e.s.d.'s in parentheses)*

Symmetry operators

	x	y	z
n^{I}	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
n^{II}	$\frac{1}{2}-x$	$1-y$	$1-z$
n^{III}	x	y	$-1+z$
n^{IV}	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
n^{V}	$-x$	$1-y$	$1-z$

Table 7 (*cont.*)

Contacts between chains

$C(1)-H(6^{I})$	2·85 (0·17) Å
$N(1)-H(6^{I})$	2·42 (0·17)
$H(3)-H(12^{I})$	2·21 (0·26)
$H(8)-H(11^{II})$	2·12 (0·29)

Contacts between planes

$C(1)-H(12^{IV})$	2·92 (0·20) Å
$N(2)-H(4^{V})$	2·75 (0·19)
$H(11)-H(8^{III})$	2·10 (0·28)

Thermal motion

The principal axis of vibration ellipsoids is given in Table 8. The reference system of axis is defined for each particular case, except for all atoms of the complex group whose system is the same. In this latter group, the atoms preferably move in a direction perpendicular to the group plane. The amplitude of vibration in the group plane is nearly equal in all directions

Table 8. *Thermal eigenvalues for non-hydrogen atoms*

$\sqrt{\bar{U}_i^2}$ are the r.m.s. amplitudes. Angles between the principal axis of the ellipsoids and reference axis are also given.

	i axis	$\sqrt{\bar{U}_i^2}$ (10^3)	**l**	**il** angle	**m**	**im** angle	**n**	**in** angle
Pd	1	0·162 (1)	Pd–C(1)	46 (9)°	PdC (1) C(2′) plane	87 (1)°	⊥ **lm**	136 (9)°
	2	0·170 (1)	”	136 (9)		88 (1)	”	134 (9)
	3	0·235 (1)	”	90 (1)	”	4 (1)	”	86 (1)
C(1)	1	0·184 (13)	”	87 (6)	”	88 (4)	”	176 (6)
	2	0·261 (16)	”	166 (9)	”	104 (9)	”	94 (6)
	3	0·329 (12)	”	104 (9)	”	14 (9)	”	89 (4)
C(2)	1	0·180 (18)	”	7 (8)	”	90 (5)	”	83 (8)
	2	0·245 (12)	”	97 (8)	”	97 (11)	”	10 (9)
	3	0·293 (11)	”	91 (5)	”	7 (11)	”	83 (11)
N(1)	1	0·208 (19)	”	8 (10)	”	87 (3)	”	97 (10)
	2	0·267 (12)	”	82 (10)	”	95 (3)	”	9 (8)
	3	0·443 (13)	”	92 (3)	”	6 (3)	”	85 (3)
N(2)	1	0·184 (12)	”	90 (4)	”	90 (3)	”	179 (4)
	2	0·295 (14)	”	177 (8)	”	93 (8)	”	90 (4)
	3	0·359 (11)	”	93 (8)	”	3 (8)	”	90 (3)
C(3)	1	0·297 (17)	C(3)–C(4)	136 (18)°	⊥ C(3)–C(4)–N(3) plane	81 (14)°	”	48 (14)
	2	0·346 (22)	”	54 (18)		48 (9)	”	63 (16)
	3	0·484 (28)	”	112 (7)	”	44 (8)	”	126 (6)
C(4)	1	0·281 (16)	C(4)–N(3)	32 (44)	⊥ C(3)–C(4)–N(3) plane	97 (8)	”	121 (44)
	2	0·297 (20)	”	58 (44)		85 (11)	”	33 (43)
	3	0·387 (18)	”	86 (7)	”	9 (9)	”	98 (10)
N(3)	1	0·214 (9)	N(3)–C(5)	53 (9)	⊥ C(4)–N(3)–C(5) plane	51 (10)	”	120 (6)
	2	0·253 (12)	”	129 (11)		41 (11)	”	80 (13)
	3	0·288 (9)	”	60 (10)	”	78 (11)	”	33 (6)
C(5)	1	0·225 (13)	C(5)–N(3)	167 (6)	⊥ N(3)–C(5)–C(6) plane	83 (7)	”	80 (4)
	2	0·334 (18)	”	80 (7)		22 (12)	”	71 (12)
	3	0·411 (19)	”	83 (5)	”	110 (12)	”	21 (11)
C(6)	1	0·266 (16)	C(6)–C(5)	137 (5)	⊥ N(3)–C(5)–C(6) plane	94 (6)	”	47 (5)
	2	0·409 (24)	”	77 (24)		23 (35)	”	71 (25)
	3	0·439 (23)	”	49 (12)	”	113 (36)	”	49 (16)

for the heavy atom, whereas the C atoms move with their minimum amplitude perpendicular to the Pd–C direction and the N atoms move along that direction. This inversion may be influenced by the presence of H bonds. In the cation, the motion is described with accuracy but it does not obey definite laws. The N(3) atom motion is the least anisotropic and the least amplified. Amplitudes increase for the atoms at the bottom of an ethyl group.

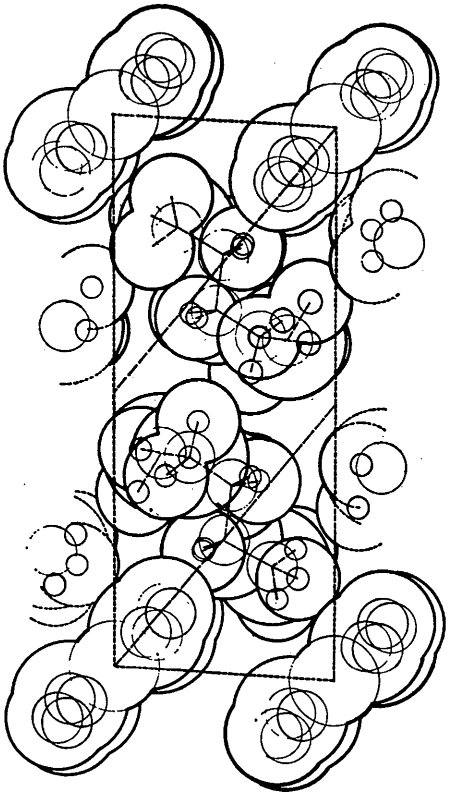

Fig. 7. Section in the structure through the (010) plane.

No attempt to correct bond lengths for thermal motion has succeeded. The approximations of riding motion and of independant vibrations have been used but it may necessitate having to account for an important libration.

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The Crystal Structure of In_6Se_7

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The crystal structure of In_6Se_7 has been determined from powder and single-crystal data and is shown to be isomorphous with that of In_6S_7. The unit cell, which contains two formula units, is monoclinic with $a=9\cdot430$, $b=4\cdot063$, $c=18\cdot378$ Å, $\beta=109\cdot34°$ and the space group is $P2_1$. Basically the structure consists of two separate sections of almost cubic close-packed arrays of Se atoms with In atoms in octahedral coordination, the two sections having equivalent directions at 61° to each other.

Introduction

In their investigations of the phases existing in the In–Se system, Slavnova, Luzhnaya & Medvedeva (1963) and Slavnova & Eliseev (1963) described a black crystalline phase to which they ascribed the formula In_5Se_6.

This phase has been examined by the author as part of an X-ray crystallographic examination of the In–Se system. The structural analysis of the phase shows that