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The Crystal and Molecular Structure of Tetrakispyrazole-nickel Chloride, $Ni(C_3H_4N_2)_4Cl_2$

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The crystal and molecular structure of tetrakispyrazole-nickel chloride, $Ni(C_3H_4N_2)_4Cl_2$, was determined by single-crystal X-ray diffraction techniques. $Ni(C_3H_4N_2)_4Cl_2$ crystallizes in the monoclinic system with $a = 13{\cdot}876 \pm 0{\cdot}001$, $b = 9{\cdot}263 \pm 0{\cdot}006$, $c = 14{\cdot}451 \pm 0{\cdot}003$ Å, $\beta = 116{\cdot}83 \pm 0{\cdot}01°$, space group $C2/c$, $\varrho_o = 1{\cdot}61$ g.cm^{-3} and $Z = 4$. Three-dimensional data (2401 reflections) were used and the structure solved by an analysis of the Patterson map. The $Ni(C_3H_4N_2)_4Cl_2$ molecule is centrosymmetric with the nickel atom at the center of an octahedron formed by two chlorine atoms and a nitrogen atom from each of the four pyrazole molecules. One pair of coordinated nitrogen atoms lies 2·097 Å and the other pair 2·087 Å from the nickel atom. The nickel–chlorine vector makes an angle of 0·4° with the normal to the plane of the coordinating nitrogen atoms and the chlorine atoms lie 2·507 Å from the nickel atom. The pyrazole rings were found to be planar within experimental error. Final refinement by a three-dimensional anisotropic least-squares analysis resulted in an R value of 5·4%.

Introduction

Electronic absorption spectra of transition element complexes have provided much information on the electron energy levels in these interesting materials (McClure, 1959). The electron paramagnetic resonance technique, where applicable, has yielded detailed accounts of the interactions between paramagnetic ions and their immediate environments (Low, 1960). In order to classify electronic transitions by symmetry type and to interpret magnetic data, however, the structure of the transition element complex must be known.

Tetrakispyrazole-nickel chloride, $Ni(C_3H_4N_2)_4Cl_2$, is a stable complex of $NiCl_2$ and pyrazole. The complex was found to be paramagnetic with a magnetic susceptibility corresponding to two unpaired electrons per nickel ion. Preliminary electronic absorption spectra of $Ni(C_3H_4N_2)_4Cl_2$ suggest a tetragonal or lower symmetry component in the ligand field of the nickel ion. The present structure determination was undertaken to provide the basis for a thorough account of low temperature optical and magnetic spectra.

Experimental

Crystals of $Ni(C_3H_4N_2)_4Cl_2$ were grown by slow evaporation of an aqueous solution of $NiCl_2$ and pyrazole. Cell data were obtained from zero and upper level precession photographs taken with Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation. Systematic extinctions (hkl, $h+k=2n+1$; $00l$, $l=2n+1$) are consistent with the monoclinic space groups Cc and $C2/c$. The space group $C2/c$ was assigned on the basis of the complete structure determination.

To determine precise unit-cell parameters, a single crystal was mounted on a diffractometer and eleven strong reflections in the 2θ range 126–152° were measured with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54051$ Å). The cell parameters were refined by least squares to obtain the best agreement between observed and calculated 2θ angles. From these refined cell parameters, and assuming $Z = 4$, the X-ray density was calculated to be 1·611 g.cm^{-3}. This compares with the observed density of 1·61 g.cm^{-3} which was measured by flotation. A summary of the crystal data is given in Table 1.

Table 1. *Crystal data for* $Ni(C_3H_4N_2)_4Cl_2$

$a = 13{\cdot}876 \pm 0{\cdot}001$ Å	Space group $C2/c$
$b = 9{\cdot}263 \pm 0{\cdot}006$	$Z = 4$
$c = 14{\cdot}451 \pm 0{\cdot}003$	$\varrho_o = 1{\cdot}61$ g.cm^{-3}
$\beta = 116{\cdot}83 \pm 0{\cdot}01°$	$\varrho_c = 1{\cdot}611$

Systematic extinctions

hkl	$h+k=2n+1$
$00l$	$l=2n+1$

For the structure determination the stationary-crystal stationary-counter method was employed. A nearly spherical crystal, 0·6 mm in diameter, was mounted on a diffractometer. The intensities of all 2401 unique reflections within $\sin\theta/\lambda = 0{\cdot}7035$ Å^{-1} were measured with a counter diffractometer using molybdenum radiation and a β-filter of 0·025 mm thick niobium. The detector was a scintillation counter equipped with a pulse-height analyzer. Attenuation filters (niobium) were used on any reflection for which the maximum counting rate exceeded 20,000 counts per second. Thus, coincidence losses were kept below two per cent.

A wavelength of 0·710688 Å, the weighted average for $K\alpha_1$ and $K\alpha_2$, was used for calculating 2θ settings for measuring peak intensities. Background readings were taken at $2\theta - \frac{1}{2}\Delta 2\theta$ and at $2\theta + \frac{1}{2}\Delta 2\theta$ where

$$\Delta 2\theta = 1{\cdot}80 + 1{\cdot}0 \tan\theta$$

is the scan range recommended by Alexander & Smith (1962). The counting time was 10 seconds for a peak and each background.

In order to convert observed intensities (I_o) to integrated intensities (I_i), strong reflections spanning the entire 2θ range were also measured by the 2θ scan method. A curve of I_i/I_o *versus* 2θ was prepared and utilized to obtain the conversion for each reflection.

The measured intensities were corrected for absorption assuming a spherical crystal with $\mu R = 0{\cdot}5$. Lorentz and polarization factors were applied in the usual manner.

Determination of the structure

As noted above, the systematic extinctions are consistent with the space groups *Cc* and *C*2/*c* which have a fourfold and an eightfold general position respectively. The unit cell was found to contain four molecules. Accordingly, if the structure belongs to the space group *Cc* each molecule would lie in a general position while if it belongs to the space group *C*2/*c* a special position problem is indicated. The data strongly suggest a special position problem (*C*2/*c*) because the observed intensities for *l* even exceed, on the average, those for which *l* is odd.

A three-dimensional Patterson map was calculated from the complete set of data. Analysis of this map led to the conclusion that the principal vectors could be accounted for on the basis of the *C*2/*c* space group with nickel at the origin. In this position the nickel atoms do not contribute to reflections with *l* odd, which accounts for the above mentioned intensity variation. As the origin is a center of symmetry, the asymmetric unit consists of one-half of a nickel atom, two independent pyrazole rings (hereafter designated ring I and ring II) and a chlorine atom. A set of vectors, corresponding to those between nickel and the atoms in its coordination sphere was identified about the origin.

An electron-density map, with phases calculated from a trial model consisting of nickel and the atoms in its coordination sphere, was then calculated. From this map two groups of five atoms corresponding to pyrazole rings I and II were identified. Each ring was apparently planar with every atom roughly equidistant from its two nearest neighbors. One problem remained – the identity of the peaks forming the rings. Since pyrazole contains two adjacent nitrogen atoms, one of which is coordinated to the nickel atom, this problem reduced to identifying the second nitrogen atom in each ring. It was tentatively assigned on the basis of the peak size in the electron density map.

Refinement

Full-matrix isotropic least-squares refinement on all atoms except hydrogen was then carried out on the trial model. Scattering factors for neutral nickel, chlorine, nitrogen, hydrogen and carbon atoms were taken from *International Tables for X-ray Crystallography* (1962). The quantity minimized in this refinement was $\Sigma w(|F_o|-|F_c|)^2$ with the following weighting scheme: $w=1$ for $|F_o|<44$ and $w=44/|F_o|$ for $|F_o|>44$. Reflections for which the net number of counts observed did not exceed zero by at least twice the standard deviation were tagged and assigned a value for the net number of counts equal to one standard deviation. These reflections were given zero weight in the refinement unless the value of F_c exceeded that of F_o. Those reflections for which this occurred were given unit weight. As a result of the refinement the agreement factor, *R*, where

$$R=\Sigma\,|F_o|-|F_c|/\Sigma\,|F_o|\,,$$

based upon 2072 observed reflections refined to a value of 0·085.

An electron-density map, with phases calculated from the refined model, showed that the ring atoms which had been tentatively identified as nitrogen atoms gave larger peaks than those identified as carbon atoms. Bond lengths and angles computed from the refined model revealed that both rings deviated from a regular pentagonal configuration. The crystallographically independent pyrazole rings, however, showed similar deviations. In an effort to verify that the bond distances and angles were not themselves dependent upon the tentative assignment of the non-coordinated nitrogen atoms a refinement was undertaken assuming that each ring contained a coordinating nitrogen atom and four, rather than three, carbon atoms. As expected, the new set of atomic parameters was identical with the first set within the standard deviations on these parameters. Moreover, the largest peaks in an electron-density map based on this model corresponded to the atoms which had been assumed to be the non-coordinated nitrogen in each ring. All the foregoing evidence leads to the conclusion that the tentative assignment of nitrogen and carbon atoms was correct.

A difference electron density (F_o-F_c) map was then calculated. The dominant features in this map were peaks which occurred in the periphery of the pyrazole rings. About each pyrazole ring, peaks corresponding to reasonable hydrogen positions were located near each carbon and the non-coordinated nitrogen atoms. This placement of hydrogen atoms in each ring requires that the coordinating nitrogen atom be of the aza type, *i.e.* it must have the –N= configuration. Full-matrix isotropic least-squares refinement of the hydrogen positions gave mixed results. Specifically, in each ring the hydrogen atoms located on atoms adjacent to the coordinating nitrogen atom refined to unrealistically short distances (0·7–0·85 Å). In contrast, hydrogen atoms located on the remaining two carbon atoms refined to more typical C–H bond distances (~1 Å). Because the overall result of refinement of the hydrogen atom positions was inconclusive, hydrogen atoms were symmetrically placed at 1·03 Å from the ring atoms. Including them lowered the *R* value from 0·085 to 0·081. In all subsequent calculations contributions from these hydrogen atoms were included in the structure factors but their coordinates and temperature factors were held constant.

The structure was next refined by the full-matrix anisotropic least-squares method. After two cycles, the R value diminished from 0·081 to 0·054. Significantly, the reflections in the higher $\sin\theta/\lambda$ region showed a much greater improvement in R. This effect was most pronounced for reflections with l odd (nickel contributes to l even only).

As a final test of the validity of the assignment of the non-coordinating nitrogen atoms a full-matrix anisotropic least-squares refinement was carried out after interchanging N(2) and C(3) in ring I and N(4) and C(6) in ring II. This interchange of assignments resulted in an increase in the R value from 0·054 to 0·063 based upon all observed reflections. This increase was observed in all regions of $\sin\theta/\lambda$ as well as in 73 of the 76 possible categories of reflections ($0kl, 1kl \ldots hk0, hk1 \ldots h0l, h1l \ldots$) including all 58 categories with 50 or more reflections. More significantly, the R value increased from 0·054 to 0·073 based on 247 observed reflections in the $\sin\theta/\lambda$ region from 0 to 0·32 where the difference between the scattering factor curves for carbon and nitrogen is greatest. Thus all of the crystallographic evidence supports the original assignment of the non-coordinating nitrogen atoms.

A final difference Fourier synthesis was computed and no spurious peaks were noted. In Table 2 final positional parameters are given and the anisotropic thermal parameters are listed in Table 3. Table 4 lists the observed and calculated structure factors.

Table 2. *Atomic coordinates*

	X/a	Y/b	Z/c
Ni	0	0	0
Cl	0·07602 (6)*	−0·16005 (8)	−0·09083 (6)
N(1)	0·14487 (20)	−0·01909 (25)	0·13696 (19)
N(2)	0·16264 (24)	0·04647 (33)	0·22631 (22)
C(3)	0·23328 (25)	−0·09518 (34)	0·15694 (27)
C(1)	0·26175 (31)	0·01280 (44)	0·30300 (28)
C(2)	0·30862 (28)	−0·07843 (41)	0·26037 (33)
N(3)	0·05581 (20)	0·18193 (27)	−0·04625 (20)
N(4)	0·11275 (27)	0·16892 (33)	−0·10013 (27)
C(5)	0·09087 (30)	0·39930 (34)	−0·09126 (30)
C(4)	0·13445 (38)	0·29716 (41)	−0·12827 (38)
C(6)	0·04254 (27)	0·32240 (34)	−0·04081 (27)

* The numbers in parentheses are standard deviations in the last significant figures.

Discussion of the structure

The only crystallographic restriction on the molecule of $Ni(C_3H_4N_2)_4Cl_2$ is that it must have a center of symmetry. The asymmetric unit, therefore, comprises one-half of a nickel atom, one chlorine atom and two independent pyrazole rings.

The crystal structure consists of discrete molecules of $Ni(C_3H_4N_2)_4Cl_2$ packed in a C-centered monoclinic cell. Symmetry relationships between molecules and the closest intermolecular approaches are shown in Fig. 1.

The molecular structure of $Ni(C_3H_4N_2)_4Cl_2$ is shown in detail in Fig. 2. Principal bond distances are indicated on Fig. 2 and principal pyrazole ring angles are given in Table 5. Fig. 3 illustrates the octahedral coordination of the nickel atom and includes only unique bond angles and distances. The pyrazole rings were found by least-squares analysis to be planar. Individual atom deviations from the least-squares planes are presented in Table 6. These deviations are all less than the average σ normal to the planes (0·003 Å) of the ring atoms.

In order to describe the details of the $Ni(C_3H_4N_2)_4Cl_2$ molecule it is convenient to use the rigorous plane defined by the coordinating pyrazole nitrogen atoms [N(1)N(1′) N(3)N(3′)] as a plane of reference. This plane, with the nickel atom at its center, may be called the basal plane. Each of the pyrazole rings intersects this basal plane and the chlorine atoms lie above and below this plane of reference. The nickel–chlorine bond makes an angle of 0·4° with the normal to the basal plane. Three parameters are needed to specify the orientation of each pyrazole ring relative to the basal plane. The first parameter is defined as the angle between the plane of the pyrazole ring and the basal plane. The second parameter is defined as the angle between the nickel–nitrogen bond and the normal to the pyrazole ring. The third parameter is defined as the perpendicular distance from the ring centroid to the basal plane. The values of these parameters for each pyrazole ring are reported in Table 7.

The pyrazole rings in this structure analysis have been determined with a precision (average bond $\sigma =$

Table 3. *Anisotropic thermal parameters**

The general anisotropic temperature factor has the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.
The numbers in parentheses are standard deviations in the last significant figures.

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Cl	646 (5)	858 (8)	598 (5)	29 (5)	355 (4)	−33 (5)
N(1)	478 (15)	758 (27)	478 (14)	−22 (16)	190 (12)	35 (15)
N(2)	666 (20)	1097 (33)	515 (17)	−12 (21)	211 (15)	−7 (20)
C(1)	708 (25)	1375 (52)	526 (20)	−184 (29)	105 (18)	79 (26)
C(2)	527 (21)	1181 (44)	841 (27)	33 (25)	115 (20)	303 (28)
C(3)	485 (18)	879 (33)	678 (21)	9 (20)	258 (16)	42 (22)
N(3)	492 (15)	810 (27)	509 (15)	−31 (17)	247 (12)	5 (17)
N(4)	943 (24)	935 (34)	1034 (25)	−28 (23)	739 (22)	75 (24)
C(4)	1091 (35)	1082 (42)	1128 (35)	−22 (31)	798 (31)	196 (31)
C(5)	776 (26)	802 (33)	855 (26)	−10 (23)	454 (22)	163 (24)
C(6)	650 (21)	762 (32)	705 (22)	−2 (21)	359 (18)	40 (22)

* The isotropic temperature factor for nickel is 2·42.

Table 4. *Observed and calculated structure factors* (× 10)

Reflections for which the net number of counts observed did not exceed zero by at least twice the standard deviation are starred. The value assigned to these reflections is equal to the standard deviation.

	F_o	F_c
H,0,0		
2	1246	1147
4	49	-56
6	154	-93
8	267	263
10	137	146
12	476	487
14	329	330
16	161	177
H,0,2		
0	1209	1145
2	3421	4081
4	2076	2214
6	135	138
8	44	-27
10	51	0
12	223	247
14	168	190
16	160	181
-2	1471	1393
-4	1376	-1252
-6	105	79
-8	712	713
-10	869	845
-12	243	233
-14	384	383
-16	98	87
-18	89	104
H,0,4		
0	217	-182
2	1711	2073
4	1603	1804
6	1201	1257
8	102	97
10	188	190
12	54	-25
14	56	79
-2	1181	-1301
-4	824	825
-6	1115	1136
-8	549	554
-10	705	702
-12	478	481
-14	75	-48
-16	193	209
-18	129	149
H,0,6		
0	328	-290
2	47	-26
4	1071	1114
6	735	758
8	755	784
10	173	183
12	26*	26
14	29*	33
-2	446	477
-4	1252	1310
-6	758	806
-8	855	887
-10	67	75
-12	254	243
-14	258	266
-16	214	219
-18	236	266
H,0,8		
0	664	673
2	18*	33
4	123	-118
6	585	640
8	423	467
10	226	261
12	149	158
-2	811	866
-4	686	728
-6	760	818
-8	59	51
-10	306	298
-12	179	185
-14	543	547
-16	377	382
-18	208	210
H,0,10		
0	537	573
2	180	196
4	228	249
6	46	69
8	129	168
10	210	249
-2	944	992
-4	260	282
-6	104	-84
-8	365	366
-10	356	366
-12	626	629
-14	491	498
-16	349	334
-18	80	81
H,0,12		
0	369	391
2	522	549
4	148	176
6	59	61
8	81	95
-2	59	65
-4	268	280
-6	107	123
-8	239	275
-10	794	813
-12	636	658
-14	228	225
-16	116	115
-18	40	29
H,0,14		
0	190	204
2	164	196
4	205	218
6	129	138
-2	51	33
-4	23*	-2
-6	445	486
-8	661	705
-10	430	449
-12	300	313
-14	148	150
-16	58	-64
-18	28*	26
H,0,16		
0	27*	22
2	51	67
-2	107	114
-4	297	302
-6	460	453
-8	453	462
-10	258	284
-12	36	-30
-14	26*	25
-16	84	71
H,0,18		
0	29*	54
-2	224	226
-4	296	302
-6	308	304
-8	155	154
-10	26*	17
-12	41	51
-14	27*	20
H,-1,0		
1	1914	1850
3	529	467
5	357	343
7	751	751
9	250	247
11	259	256
13	471	484
15	186	199
17	105	116
H,-1,1		
1	143	146
3	552	522
5	151	-141
7	17*	-32
9	120	112
11	312	324
13	25*	4
15	47	-57
-1	392	-357
-3	426	-387
-5	271	255
-7	471	-445
-9	510	-495
-11	21*	-10
-13	135	126
-15	194	200
-17	54	56
H,-1,2		
1	743	694
3	1179	1158
5	1115	1145
7	187	196
9	212	209
11	301	311
13	166	185
15	167	181
-1	1429	1315
-3	813	811
-5	259	223
-7	345	335
-9	949	929
-11	481	469
-13	236	247
-15	334	322
-17	94	103
H,-1,3		
1	298	-328
3	392	387
5	267	276
7	175	-177
9	21*	-16
11	58	54
13	95	112
15	28*	24
-1	592	-557
-3	579	549
-5	1044	-1010
-7	649	-633
-9	134	-134
-11	385	358
-13	329	325
-15	120	114
-17	47	-29
H,-1,4		
1	696	686
3	1226	1246
5	506	509
7	614	620
9	232	246
11	174	186
13	92	102
15	98	116
-1	213	230
-3	613	569
-5	917	954
-7	786	753
-9	536	550
-11	681	696
-13	314	303
-15	79	87
-17	142	143
H,-1,5		
1	43	41
3	123	-127
5	289	286
7	100	115
9	56	-71
11	53	-56
13	27*	35
-1	184	-190
-3	991	-1086
-5	604	-635
-7	189	-178
-9	608	596
-11	457	475
-13	199	194
-15	87	-96
-17	107	-115
H,-1,6		
1	744	715
3	300	314
5	677	681
7	318	323
9	407	431
11	128	143
13	53	64
-1	155	174
-3	840	876
-5	921	958
-7	907	934
-9	499	507
-11	366	379
-13	302	298
-15	173	170
-17	115	125
H,-1,7		
1	477	-457
3	18*	10
5	72	62
7	186	186
9	39	46
11	27*	-21
13	29*	-22
-1	462	-458
-3	635	-629
-5	151	-141
-7	749	744
-9	702	666
-11	168	157
-13	117	-127
-15	188	-190
-17	125	-128
H,-1,8		
1	330	351
3	296	298
5	160	176
7	407	442
9	195	220
11	94	112
-1	931	949
-3	493	515
-5	835	880
-7	571	578
-9	510	508
-11	204	214
-13	327	317
-15	218	209
-17	248	238
H,-1,9		
1	295	-294
3	267	-267
5	23*	-34
7	74	73
9	76	87
11	46	45
-1	449	-465
-3	96	91
-5	619	652
-7	622	602
-9	140	128
-11	117	-110
-13	310	-327
-15	125	-116
-17	51	43
H,-1,10		
1	308	313
3	261	286
5	269	286
7	109	133
9	44	80
-1	631	686
-3	770	789
-5	193	221
-7	406	422
-9	419	430
-11	351	360
-13	181	176
-15	386	401
-17	171	170
H,-1,11		
1	202	-197
3	215	-211
5	139	-140
7	46	-50
9	50	54
-1	119	123
-3	425	424
-5	422	420
-7	122	122
-9	191	-182
-11	309	-334
-13	72	-75
-15	43	46
-17	127	126
H,-1,12		
1	512	505
3	301	314
5	142	157
7	27*	57
-1	164	171
-3	378	413
-5	387	380
-7	236	260
-9	312	306
-11	437	444
-13	346	342
-15	145	145
-17	147	170
H,-1,13		
1	94	94
3	44	-65
5	131	-126
7	69	-61
-1	244	251
-3	231	224
-5	91	83
-7	207	-211
-9	223	-215
-11	77	-87
-13	78	97
-15	154	150
-17	26*	-16
H,-1,14		
1	176	203
3	194	208
5	119	136
-1	304	322
-3	23*	21
-5	363	359
-7	344	360
-9	316	346
-11	203	218
-13	321	330
-15	90	97
-17	27*	-1
H,-1,15		
1	111	116
3	55	49
5	29*	-15
-1	122	131
-3	24*	10
-5	162	-160
-7	103	-100
-9	25*	-64
-11	123	123
-13	116	119
-15	26*	-21
-17	113	-115
H,-1,16		
1	101	113
3	100	113
-1	101	110
-3	265	262
-5	167	177
-7	321	329
-9	252	256
-11	227	214
-13	26*	25
-15	125	118
-17	84	84
H,-1,17		
1	63	56
-1	28*	-30
-3	59	-54
-5	64	-59
-7	25*	-21
-9	116	105
-11	93	86
-13	61	-51
-15	137	-132
H,-1,18		
-1	117	126
-3	190	188
-5	197	207
-7	156	158
-9	142	150
-11	79	86
-13	68	72
-15	79	78
H,-1,19		
-3	30*	-36
-5	29*	24
-7	64	58
-9	28*	35
-11	59	-57
-13	107	-99
H,-2,0		
0	1176	1160
2	569	-524
4	982	960
6	1102	1146
8	800	796
10	351	336
12	358	366
14	162	174
16	94	99
H,-2,1		
0	250	266
2	93	-96
4	870	-837
6	357	-336
8	64	58
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12	199	215
14	49	-38
16	87	-90
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-6	38	13
-8	482	-455
-10	231	-243
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-14	213	204
-16	57	50
H,-2,2		
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6	659	656
8	545	542
10	458	471
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14	138	156
16	70	80
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-4	850	835
-6	735	710
-8	865	837
-10	653	643
-12	62	65
-14	258	257
-16	177	174
H,-2,3		
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2	709	691
4	111	-76
6	314	-310
8	427	-417
10	127	135
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14	57	77
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-4	140	-126
-6	712	-680
-8	383	-379
-10	206	187
-12	382	354
-14	110	114
-16	27*	2
-18	133	-147
H,-2,4		
0	1109	1167
2	571	551
4	121	-18
6	351	343
8	270	288
10	434	447
12	245	255
14	143	171
-2	799	808
-4	1302	1423
-6	890	873
-8	473	470
-10	466	461
-12	427	427
-14	139	135
-16	225	243
-18	130	126
H,-2,5		
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2	506	491
4	416	407
6	63	-66
8	59	-42
10	238	-249
12	26*	-9
14	64	59
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-4	580	-627
-6	405	-393
-8	396	351
-10	412	414
-12	330	342
-14	143	-130
-16	249	-254
-18	63	-55
H,-2,6		
0	973	998
2	747	754
4	440	455
6	75	-55
8	312	317
10	165	185
12	148	172
-2	758	761
-4	830	850
-6	741	775
-8	651	663
-10	245	270
-12	446	443
-14	343	350
-16	98	94
-18	101	108
H,-2,7		
0	420	-404
2	104	-117
4	342	346
6	281	294
8	61	-10
10	54	-64
12	28*	-41
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-4	371	-347
-6	415	396
-8	632	619
-10	465	439
-12	359	-359
-14	282	-280
-16	139	-149
-18	27*	16
H,-2,8		
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2	648	673
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6	379	408
8	91	90
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12	101	119
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-4	488	509
-6	778	804
-8	425	439
-10	539	547
-12	274	282
-14	240	237
-16	132	128
-18	90	83
H,-2,9		
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2	161	-156
4	105	-110
6	145	146
8	133	137
10	27*	49
-2	29	-31
-4	360	351
-6	608	601
-8	317	304
-10	301	-313
-12	408	-415
-14	257	-254
-16	126	121
-18	102	107
H,-2,10		
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2	195	214
4	482	527
6	187	219
8	86	104
10	90	100
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-4	503	529
-6	310	337
-8	666	689
-10	342	352
-12	162	172
-14	92	113
-16	198	186
-18	130	130
H,-2,11		
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2	257	-262
4	136	-135
6	43	-45
8	46	42
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-4	545	505
-6	156	145
-8	240	-260
-10	499	-559
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-14	170	161
-16	154	160
-18	67	48
H,-2,12		
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6	134	156
8	132	154
-2	302	310
-4	604	599
-6	469	483
-8	153	158
-10	265	272
-12	161	173
-14	128	131
-16	184	179
-18	209	207
H,-2,13		
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2	56	59
4	84	-89
6	106	-112
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-6	193	-201
-8	453	-464
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-12	157	157
-14	248	235
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-18	29*	-10
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6	107	129
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-4	225	247
-6	298	321
-8	173	188
-10	66	14
-12	233	247
-14	257	262
-16	154	163
-18	186	181
H,-2,15		
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2	108	97
4	28*	7
-2	26*	44
-4	208	-210
-6	264	-259
-8	48	-71
-10	182	175
-12	204	198
-14	27*	25
-16	50	-53
H,-2,16		
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2	141	145
-2	219	223
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-6	44	55
-8	129	136
-10	220	231
-12	159	160
-14	220	226
-16	237	226
H,-2,17		
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-2	127	-116
-4	97	-92
-6	73	-70
-8	162	152
-10	160	143
-12	26*	25
-14	108	-115
-16	29*	-36
H,-2,18		
-4	51	59
-6	102	93
-8	134	141
-10	196	205
-12	203	206
-14	152	149
H,-2,19		
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-10	28*	-6
-12	92	-88
H,-3,0		
1	266	238
3	372	322
5	1245	1276
7	1439	1469
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11	177	169
13	84	84
15	80	90
H,-3,1		
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7	58	53
9	272	-264
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15	53	48
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-7	137	112
-9	40	-54
-11	53	49
-13	133	-140
-15	50	41
-17	29*	-5
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3	194	-159
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7	605	615
9	750	753
11	390	389
13	182	185
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-13	85	76
-15	216	215
-17	191	194
H,-3,3		
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3	192	211
5	71	-67
7	163	-169
9	81	99
11	92	-99
13	26*	10
15	28*	22
-1	577	-520
-3	867	838
-5	250	-247
-7	281	229
-9	170	-152
-11	72	-83
-13	24*	11
-15	26*	9
-17	28*	3
H,-3,4		
1	645	638
3	445	443
5	96	-73
7	315	309
9	430	431
11	431	450
13	202	208
-1	1507	1705
-3	1403	1536
-5	1066	1083
-7	231	-202
-9	131	130
-11	361	361
-13	304	303
-15	202	213
-17	250	254
H,-3,5		
1	342	332
3	214	-195
5	42	33
7	21*	37
9	58	-47
11	57	-41
13	28*	2
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-3	306	-333
-5	590	598
-7	317	-313
-9	90	-105
-11	21*	-30
-13	86	86
-15	40	-50
-17	28*	19
H,-3,6		
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3	589	583
5	161	171
7	52	60
9	189	213
11	180	207
13	157	180
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-3	613	617
-5	109	-111
-7	351	349
-9	345	342
-11	486	492
-13	414	406
-15	318	316
-17	95	99
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7	23*	16
9	24*	-26
11	27*	-2
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-3	216	208
-5	397	-390
-7	18*	-31
-9	64	53
-11	39	-40
-13	23*	-13
-15	44	30
-17	53	-36
H,-3,8		
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5	407	419
7	213	231
9	45	47
11	55	48
-1	552	534
-3	224	-194
-5	246	264
-7	664	666
-9	669	647
-11	377	365
-13	397	379
-15	200	197
-17	82	75
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3	55	-65
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7	24*	8
9	26*	-8
11	28*	14
-1	121	-127
-3	18*	-1
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-7	58	-74
-9	20*	-34
-11	122	112
-13	109	-124
-15	41	54
-17	47	24
H,-3,10		
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5	429	449
7	197	219
9	63	71
-1	86	112
-3	340	338
-5	471	479
-7	677	660
-9	545	545
-11	291	294
-13	161	156
-15	119	117
-17	125	117
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3	68	59
5	25*	14
7	27*	-30
9	29*	34
-1	38	33
-3	71	-81
-5	38	-59
-7	65	60
-9	21*	-23
-11	103	-110
-13	135	125
-15	25*	-46
-17	27*	34
H,-3,12		
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3	138	161
5	162	195
7	137	162
-1	56	52
-3	532	552
-5	695	693
-7	292	305
-9	184	176
-11	273	280
-13	97	91
-15	106	106
-17	281	282
H,-3,13		
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5	27*	-15
7	30*	34
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-3	58	-60
-5	80	77
-7	95	-98
-9	22*	3
-11	60	40
-13	24*	-4
-15	60	41
-17	28*	-1
H,-3,14		
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3	51	63
5	28*	53
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-5	330	317
-7	202	208
-9	90	90
-11	72	76
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-15	312	304
-17	256	256
H,-3,15		
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-3	25*	-0
-5	96	-93
-7	65	63
-9	23*	-6
-11	38	31
-13	26*	3
-15	28*	27
-17	29*	-2
H,-3,16		
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3	86	87
-1	239	255
-3	223	231
-5	25*	26
-7	82	86
-9	162	158
-11	222	212
-13	293	279
-15	352	333
H,-3,17		
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-1	60	-55
-3	27*	20
-5	26*	12
-7	26*	-29
-9	66	52
-11	27*	14
-13	28*	-3
-15	28*	-1
H,-3,18		
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-3	44	53
-5	60	57
-7	87	86
-9	228	224
-11	289	278
-13	274	255
H,-3,19		
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-7	29*	29
-9	28*	-12
-11	29*	-2
H,-4,0		
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2	224	198
4	708	685
6	1151	1133
8	740	728
10	162	146
12	164	159
14	149	155
16	88	104
H,-4,1		
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2	157	134
4	152	161
6	224	223
8	82	93
10	175	-166
12	24*	-14
14	26*	-25
16	28*	26
-2	109	-130
-4	265	-255
-6	17*	-8
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-10	145	136
-12	[illegible]	31
-14	112	-115
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2	167	-138
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6	719	697
8	491	477
10	500	498
12	214	210
14	101	98
-2	1417	1404
-4	1216	1187
-6	697	677
-8	437	405
-10	251	238
-12	110	114
-14	215	214
-16	242	245
H,-4,3		
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2	266	-255
4	59	58
6	104	111
8	22*	39
10	206	209
12	103	-108
14	48	-51
-2	44	-45
-4	245	222
-6	64	36
-8	197	174
-10	85	77
-12	238	-232
-14	155	-181
-16	81	62
H,-4,4		
0	930	913
2	376	395
4	235	226
6	57	60
8	382	384
10	357	365
12	250	262
14	110	112
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-4	1182	1228
-6	136	139
-8	136	119
-10	337	331
-12	440	447
-14	250	252
-16	189	190
H,-4,5		
0	266	259
2	200	-188
4	342	-346
6	110	-98
8	200	209
10	25*	-7
12	43	49
-2	49	-50
-4	111	110
-6	330	338
-8	31	7
-10	415	-459
-12	141	-149
-14	71	50
-16	121	123
-18	124	123
H,-4,6		
0	1052	1069
2	831	817
4	301	301
6	57	63
8	177	178
10	166	180
12	158	175
-2	668	648
-4	113	125
-6	377	386
-8	299	320
-10	543	561
-12	423	418
-14	335	341
-16	98	97
-18	57	67
H,-4,7		
0	193	203
2	49	-51
4	58	-69
6	112	-124
8	140	-128
10	26*	40
12	65	74
-2	328	315
-4	17*	15
-6	70	-97
-8	328	-332
-10	230	-249
-12	23*	-41
-14	377	355
-16	161	149
-18	28*	-22
H,-4,8		
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2	705	704
4	334	334
6	349	366
8	69	72
10	56	70
-2	264	276
-4	45	28
-6	497	522
-8	746	762
-10	447	441
-12	349	351
-14	183	170
-16	112	109
-18	28*	32
H,-4,9		
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2	298	303
4	24*	19
6	83	-80
8	83	-85
10	45	-30
-2	69	59
-4	41	-59
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-8	365	-392
-10	163	155
-12	455	437
-14	128	108
-16	26*	3
-18	28*	-56
H,-4,10		
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2	138	144
4	479	519
6	208	237
8	122	131
-2	145	147
-4	544	561
-6	473	480
-8	627	632
-10	358	360
-12	163	139
-14	68	71
-16	136	121
-18	148	148
H,-4,11		
2	46	24
4	152	150
6	27*	42
8	28*	-40
-2	182	-202
-4	198	-198
-6	246	-265
-8	195	188
-10	334	340
-12	244	226
-14	24*	-51
-16	115	-129
-18	67	-64
H,-4,12		
0	57	30
2	210	220
4	122	143
6	136	156
-2	374	373
-4	538	533
-6	553	553
-8	119	131
-10	239	241
-12	105	92
-14	125	121
-16	160	156
-18	226	231
H,-4,13		
0	117	-117
2	25*	3
4	27*	33
6	29*	41
-2	161	-148
-4	124	-134
-6	181	166
-8	286	278
-10	227	203
-12	101	-116
-14	120	-123
-16	58	-69
H,-4,14		
0	277	286
2	103	112
4	28*	35
-2	319	323
-4	305	313
-6	219	245
-8	146	154
-10	24*	7
-12	197	200
-14	227	228
-16	220	228
H,-4,15		
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2	88	-83
-2	26*	2
-4	61	45
-6	203	204
-8	161	144
-10	96	-106
-12	135	-149
-14	27*	-34
-16	28*	19
H,-4,16		
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2	89	105
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-4	139	147
-6	37	34
-8	123	139
-10	159	158
-12	199	197
-14	243	243
-16	168	157
H,-4,17		
0	30*	-23
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-4	160	156
-6	26*	13
-8	75	-70
-10	79	-90
-12	28*	-11
-14	27*	-1
H,-4,18		
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-4	46	50
-6	82	88
-8	113	108
-10	241	239
-12	189	183
H,-4,19		
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-8	63	-77
-10	28*	-15
H,-5,0		
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3	546	510
5	227	221
7	352	331
9	187	172
11	419	417
13	194	190
15	233	235

Table 4 (*cont.*)

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H,-5,1		
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7	78	92
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13	81	-74
15	28•	35
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-3	385	-394
-5	113	89
-7	284	262
-9	322	287
-11	172	159
-13	151	-161
-15	131	-138
H,-5,2		
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3	692	692
5	794	770
7	84	72
9	196	190
11	126	123
13	266	282
15	85	89
-1	626	627
-3	683	638
-5	246	-209
-7	572	535
-9	686	650
-11	338	319
-13	248	244
-15	170	154
H,-5,3		
1	363	-360
3	50	62
5	20•	7
7	60	59
9	189	199
11	116	-106
13	118	-110
-1	389	-398
-3	430	408
-5	283	249
-7	508	463
-9	159	142
-11	240	-236
-13	258	-259
-15	76	-92
-17	29•	42
H,-5,4		
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3	896	879
5	557	538
7	338	340
9	132	145
11	153	158
13	56	63
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-3	86	-55
-5	939	928
-7	462	454
-9	641	631
-11	316	302
-13	244	227
-15	139	142
-17	148	149
H,-5,5		
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3	407	-406
5	220	-220
7	137	151
9	46	48
11	26•	37
13	28•	-10
-1	252	233
-3	132	132
-5	752	770
-7	65	62
-9	386	-415
-11	351	-391
-13	68	-74
-15	93	76
-17	110	108
H,-5,6		
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3	490	479
5	321	318
7	436	420
9	239	242
11	79	81
-1	68	75
-3	583	598
-5	724	749
-7	805	798
-9	140	127
-11	338	337
-13	277	279
-15	182	191
-17	74	67
H,-5,7		
1	38	28
3	21•	-1
5	119	-110
7	171	-173
9	26•	-2
11	57	52
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-5	191	-205
-7	270	-295
-9	432	-435
-11	193	-199
-13	201	177
-15	240	223
-17	50	24
H,-5,8		
1	291	291
3	47	43
5	348	354
7	248	257
9	173	185
11	98	112
-1	494	491
-3	660	665
-5	549	561
-7	324	324
-9	307	304
-11	309	301
-13	269	254
-15	206	194
-17	141	132
H,-5,9		
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3	155	159
5	24•	-20
7	91	-88
9	83	-76
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-5	272	-289
-7	557	-596
-9	68	-90
-11	378	339
-13	194	177
-15	54	27
-17	28•	-37
H,-5,10		
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3	224	243
5	137	146
7	117	136
9	105	130
-1	565	563
-3	509	518
-5	194	188
-7	194	195
-9	470	473
-11	285	278
-13	208	209
-15	156	155
-17	165	161
H,-5,11		
1	78	62
3	216	211
5	107	107
7	39	-11
-1	24•	-19
-3	320	-331
-5	344	-360
-7	38	12
-9	261	238
-11	236	218
-13	95	71
-15	136	-146
-17	80	-89
H,-5,12		
1	319	344
3	191	212
5	102	112
7	75	80
-1	240	243
-3	199	197
-5	280	274
-7	265	273
-9	325	300
-11	308	306
-13	164	173
-15	144	145
-17	54	54
H,-5,13		
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-3	195	-193
-5	49	31
-7	229	209
-9	240	207
-11	24•	-9
-13	173	-170
-15	68	-72
-17	28•	1
H,-5,14		
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3	158	170
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-3	108	107
-5	249	236
-7	352	368
-9	177	188
-11	170	183
-13	180	182
-15	63	69
H,-5,15		
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3	67	-51
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-5	128	113
-7	180	164
-9	25•	-31
-11	169	-175
-13	62	-76
-15	28•	36
H,-5,16		
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-1	108	105
-3	188	181
-5	186	195
-7	205	208
-9	205	204
-11	108	101
-13	61	64
-15	56	65
H,-5,17		
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-5	81	75
-7	92	-89
-9	92	-97
-11	46	-39
-13	28•	24
H,-5,18		
-5	162	166
-7	104	98
-9	119	117
-11	67	69
H,-6,0		
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2	1135	1094
4	236	225
6	51	42
8	189	173
10	123	89
12	236	236
14	259	251
H,-6,1		
0	116	99
2	153	-134
4	245	241
6	187	187
8	75	-62
10	139	-138
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14	29•	-14
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-4	129	-133
-6	29	-12
-8	255	234
-10	24•	27
-12	47	19
-14	46	-64
H,-6,2		
0	1074	1073
2	1161	1120
4	881	844
6	495	472
8	80	-83
10	91	81
12	92	100
14	121	134
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-4	100	-26
-6	114	108
-8	362	317
-10	440	406
-12	292	279
-14	190	176
-16	148	150
H,-6,3		
0	350	-343
2	19•	20
4	117	118
6	22•	-12
8	108	116
10	24•	40
12	79	-76
-2	161	-155
-4	192	164
-6	236	211
-8	38	15
-10	23•	11
-12	82	-92
-14	26•	21
-16	28•	-16
H,-6,4		
0	113	99
2	805	765
4	1065	1030
6	426	437
8	330	320
10	78	67
12	38	27
-2	113	11
-4	397	376
-6	372	326
-8	530	509
-10	382	364
-12	300	288
-14	120	113
-16	52	54
H,-6,5		
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2	35	-33
4	236	-224
6	74	82
8	101	105
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12	61	-17
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-6	280	281
-8	195	-206
-10	119	-137
-12	106	88
-14	25•	11
-16	27•	-16
H,-6,6		
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2	267	249
4	395	376
6	555	548
8	393	390
10	170	168
-2	166	151
-4	498	499
-6	737	736
-8	235	204
-10	319	326
-12	147	141
-14	143	149
-16	113	111
H,-6,7		
0	89	87
2	184	-189
4	23•	9
6	26•	-22
8	50	-33
10	28•	36
-2	320	303
-4	35	26
-6	301	-320
-8	94	87
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-12	23•	-6
-14	47	22
-16	28•	15
H,-6,8		
0	227	219
2	98	93
4	95	78
6	309	320
8	242	259
10	191	203
-2	635	640
-4	405	386
-6	299	292
-8	354	358
-10	66	64
-12	209	201
-14	227	211
-16	262	264
H,-6,9		
0	67	62
2	92	90
4	23•	-17
6	61	-55
8	27•	-13
-2	22•	-2
-4	63	-73
-6	63	-72
-8	22•	-35
-10	190	162
-12	24•	-9
-14	53	-58
-16	28•	-20
H,-6,10		
0	460	468
2	116	115
4	165	167
6	69	72
8	108	128
-2	309	310
-4	368	369
-6	33	20
-8	193	190
-10	292	281
-12	275	262
-14	292	297
-16	275	257
H,-6,11		
0	24•	0
2	43	55
4	26•	27
6	26•	-12
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-4	64	-84
-6	93	98
-8	126	99
-10	25•	-48
-12	25•	-15
-14	26•	-15
-16	59	-65
H,-6,12		
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2	301	312
4	144	151
6	44	50
-2	215	219
-4	24•	27
-6	222	221
-8	173	166
-10	385	385
-12	362	355
-14	276	274
-16	71	74
H,-6,13		
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-2	42	-63
-4	82	62
-6	103	93
-8	24•	-12
-10	25•	-49
-12	26•	-34
-14	27•	-50
-16	28•	10
H,-6,14		
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2	156	169
-2	25•	2
-4	121	122
-6	238	243
-8	346	357
-10	289	295
-12	257	273
-14	107	92
H,-6,15		
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-2	83	71
-4	26•	23
-6	26•	-14
-8	27•	-1
-10	46	-57
-12	55	-58
-14	27•	16
H,-6,16		
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-2	103	95
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-6	252	253
-8	311	317
-10	176	175
-12	64	62
-14	29•	16
H,-6,17		
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-6	46	-51
-8	51	-66
-10	28•	8
-12	27•	0
H,-6,18		
-8	101	102
H,-7,0		
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3	307	291
-5	124	106
-7	224	210
-9	206	186
-11	311	296
-13	194	179
H,-7,1		
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-3	126	123
-5	58	-69
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-9	229	-219
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-13	157	141
-15	73	73
1	36	33
3	87	-81
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7	22•	-25
9	116	135
11	118	141
13	28•	45
H,-7,2		
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-3	202	182
-5	67	50
-7	434	418
-9	463	422
-11	342	308
-13	240	235
-15	68	64
1	750	760
3	639	633
5	436	432
7	105	97
9	116	124
11	93	93
13	208	221
H,-7,3		
1	20•	27
3	273	263
5	70	-46
7	166	-154
9	58	69
11	66	79
13	28•	21
-1	19•	-0
-3	90	-90
-5	286	-287
-7	428	-433
-9	25•	28
-11	259	239
-13	202	183
-15	69	46
H,-7,4		
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3	708	667
5	533	501
7	248	237
9	119	116
11	134	137
-1	112	80
-3	183	182
-5	604	606
-7	361	346
-9	556	535
-11	301	298
-13	85	74
-15	51	38
H,-7,5		
1	120	123
3	73	73
5	25•	15
7	153	150
9	96	-92
11	28•	-18
-1	156	-175
-3	464	-503
-5	276	-303
-7	98	87
-9	229	219
-11	316	315
-13	110	91
-15	64	-64
H,-7,6		
1	151	137
3	207	195
5	287	270
7	371	360
9	215	213
11	64	58
-1	137	132
-3	482	495
-5	547	555
-7	645	625
-9	197	189
-11	145	145
-13	70	64
-15	96	91
H,-7,7		
1	208	-213
3	96	-94
5	217	226
7	29•	12
9	29•	27
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-3	203	-220
-5	122	-132
-7	466	450
-9	427	403
-11	43	22
-13	111	-123
-15	63	-72
H,-7,8		
1	210	208
3	43	-33
5	185	185
7	174	189
9	149	156
-1	490	482
-3	508	496
-5	456	449
-7	322	308
-9	156	149
-11	23•	-12
-13	190	160
-15	254	241
H,-7,9		
1	259	-266
3	79	-84
5	56	-57
7	62	61
-1	208	-229
-3	68	64
-5	438	437
-7	220	211
-9	141	120
-11	101	-129
-13	136	-144
-15	71	-78
H,-7,10		
1	253	248
3	197	199
5	27•	44
7	69	72
-1	443	425
-3	418	412
-5	233	218
-7	50	49
-9	94	86
-11	231	220
-13	270	259
-15	181	191
H,-7,11		
1	117	-123
3	110	-123
5	114	-107
-1	89	87
-3	230	219
-5	277	277
-7	97	76
-9	183	-206
-11	105	-121
-13	27•	-26
-15	57	56
H,-7,12		
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3	178	193
5	104	110
-1	220	217
-3	173	166
-5	94	95
-7	64	63
-9	233	217
-11	339	324
-13	223	224
-15	115	111
H,-7,13		
1	104	111
3	85	-80
-1	115	109
-3	195	187
-5	24•	-14
-7	67	-86
-9	133	-141
-11	27•	-13
-13	60	64
-15	63	50
H,-7,14		
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-1	116	111
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-7	243	238
-9	268	258
-11	201	209
-13	108	117
H,-7,15		
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-7	73	-89
-9	56	46
-11	28•	22
-13	81	54
H,-7,16		
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-5	148	144
-7	238	236
-9	188	185
-11	65	60
H,-7,17		
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H,-8,0		
0	79	54
2	212	193
-4	393	387
-6	301	289
-8	408	402
-10	231	233
-12	176	184
H,-8,1		
0	210	210
2	185	-177
4	52	-50
6	206	-207
8	121	-119
10	95	116
12	102	123
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-4	353	360
-6	45	-46
-8	109	-138
-10	131	-159
-12	26•	25
-14	28•	15
H,-8,2		
0	228	224
2	21•	-2
4	172	154
6	400	380
8	213	197
10	211	212
12	217	219
-2	432	430
-4	379	373
-6	442	444
-8	331	314
-10	331	337
-12	136	129
-14	88	89
H,-8,3		
0	19•	18
2	225	214
4	103	106
6	264	-255
8	96	-85
10	65	-49
12	29•	42
-2	250	244
-4	36	40
-6	223	-230
-8	227	-248
-10	96	75
-12	118	99
-14	129	111
H,-8,4		
0	265	239
2	199	188
4	166	147
6	96	77
8	193	180
10	224	213
-2	517	502
-4	480	467
-6	349	332
-8	425	414
-10	214	212
-12	159	148
-14	93	79
H,-8,5		
0	176	176
2	190	199
4	24•	-21
6	158	150
8	100	-86
10	98	-90
-2	110	-108
-4	299	-328
-6	22•	-28
-8	52	-9
-10	176	174
-12	159	139
-14	27•	-15
H,-8,6		
0	478	467
2	315	286
4	82	60
6	93	85
8	140	139
10	84	89
-2	263	244
-4	440	448
-6	466	477
-8	219	204
-10	183	178
-12	176	158
-14	120	126
H,-8,7		
0	80	-71
2	60	-67
4	160	158
6	101	94
8	29•	32
-2	126	-138
-4	111	-131
-6	36	-27
-8	421	401
-10	70	42
-12	26•	-46
-14	114	-127
H,-8,8		
0	289	278
2	252	241
4	195	183
6	103	104
8	52	50
-2	451	446
-4	275	261
-6	310	300
-8	283	271
-10	144	134
-12	133	134
-14	143	130
H,-8,9		
0	140	-149
2	82	-83
4	26•	6
6	44	34
-2	62	-86
-4	195	191
-6	233	218
-8	25•	3
-10	60	25
-12	186	-203
-14	133	-125
H,-8,10		
0	268	259
2	201	205
4	167	170
6	97	107
-2	247	240
-4	340	342
-6	164	156
-8	179	176
-10	211	209
-12	98	98
-14	54	62
H,-8,11		
0	39	-38
2	39	-36
4	58	-71
-2	141	138
-4	150	128
-6	116	99
-8	87	-109
-10	196	-210
-12	81	-87
-14	45	36
H,-8,12		
0	169	169
2	168	169
-2	246	236
-4	162	156
-6	210	210
-8	137	136
-10	85	95
-12	105	100
-14	94	92
H,-8,13		
0	127	119
2	28•	16
-2	69	59
-4	26•	25
-6	85	-93
-8	134	-138
-10	107	-112
-12	62	55
H,-8,14		
0	158	156
-2	106	108
-4	169	167
-6	127	121
-8	79	91
-10	76	62
-12	92	98
H,-8,15		
-2	28•	27
-4	99	-96
-6	105	-122
-8	28•	-21
-10	69	51
H,-8,16		
-6	79	75
-8	73	73
H,-9,0		
1	47	-59
-3	330	322
-5	541	533
-7	422	411
-9	234	224
-11	54	44
H,-9,1		
1	59	-50
3	207	-198
5	134	-135
7	100	-81
9	26•	14
11	28•	39
-1	232	239
-3	282	293
-5	65	-20
-7	24•	-47
-9	25•	-11
-11	27•	-53
-13	28•	2
H,-9,2		
1	47	-55
3	79	-77
5	269	246
7	404	395
9	258	258
11	166	158
-1	426	435
-3	599	615
-5	521	508
-7	225	218
-9	55	50
-11	44	16
-13	51	66
H,-9,3		
1	225	222
3	42	52
5	182	-164
7	174	-165
9	27•	-2
11	30•	17
-1	172	165
-3	24•	5
-5	89	51
-7	125	-136
-9	24•	-34
-11	44	35
-13	28•	0
H,-9,4		
1	342	314
3	101	83
5	24•	-23
7	126	113
9	227	218
-1	633	609
-3	611	590
-5	192	161
-7	34	-9
-9	46	37
-11	133	133
-13	130	133
H,-9,5		
1	201	201
3	160	162
5	73	-79
7	26•	1
9	96	-88
-1	59	29
-3	118	-118
-5	39	-47
-7	47	60
-9	25•	-56
-11	27•	14
-13	28•	11
H,-9,6		
1	637	612
3	259	245
5	66	51
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-3	138	118
-5	24•	22
-7	74	66
-9	133	113
-11	262	257
-13	230	230
H,-9,7		
1	26•	21
3	26•	14
5	174	185
7	28•	-30
-1	24•	-29
-3	23•	6
-5	76	-77
-7	63	42
-9	83	59
-11	41	-62
-13	90	-96
H,-9,8		
1	273	256
3	359	352
5	215	211
7	62	76
-1	201	183
-3	54	-55
-5	58	47
-7	225	208
-9	374	370
-11	170	172
-13	155	147
H,-9,9		
1	74	-86
3	68	73
5	29•	29
-1	24•	-19
-3	51	39
-5	67	52
-7	38	-56
-9	29•	-14
-11	89	-93
-13	28•	-33
H,-9,10		
1	72	68
3	203	205
-1	44	-22
-3	114	101
-5	230	228
-7	315	320
-9	218	210
-11	161	172
-13	28•	12
H,-9,11		
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3	28•	-5
-1	26•	10
-3	26•	-7
-5	45	37
-7	54	-58
-9	138	-143
-11	27•	-12
-13	86	58
H,-9,12		
1	28•	38
-1	68	55
-3	229	227
-5	268	268
-7	213	214
-9	94	82
-11	27•	27
H,-9,13		
-1	28•	2
-3	28•	-3
-5	86	-91
-7	27•	-39
-9	50	-57
-11	87	57
H,-9,14		
-3	170	172
-5	190	188
-7	46	34
-9	28•	33
H,-10,0		
0	230	221
-2	129	110
-4	301	296
-6	239	227
-8	283	277
10	103	97
H,-10,1		
0	23•	3
2	92	-85
4	124	142
6	94	99
8	27•	-20
10	28•	-11
-2	81	-99
-4	39	-45
-6	77	-87
-8	74	67
-10	88	82
H,-10,2		
0	198	195
2	164	156
4	95	93
6	219	203
8	224	210
10	129	121
-2	322	325
-4	295	281
-6	350	345
-8	82	66
-10	73	78
H,-10,3		
0	153	-164
2	24•	22
4	24•	-2
6	26•	-26
8	103	107
-2	69	-74
-4	24•	12
-6	110	100
-8	51	39
-10	26•	-12
-12	44	-55
H,-10,4		
0	240	219
2	259	235
4	155	144
6	94	89
8	74	61
-2	416	399
-4	322	299
-6	78	63
-8	57	50
-10	105	79
-12	133	138
H,-10,5		
0	26•	21
2	50	-51
4	140	-135
6	27•	27
8	28•	19
-2	25•	-44
-4	74	69
-6	147	144
-8	50	-58
-10	114	-123
-12	29•	-54
H,-10,6		
0	383	365
2	272	253
4	174	161
6	93	85
-2	162	141
-4	135	133
-6	41	27
-8	123	110
-10	156	150
-12	228	212
H,-10,7		
0	43	42
2	66	-73
4	27•	-5
6	43	-50
-2	140	140
-4	25•	29
-6	94	-99
-8	26•	-45
-10	100	-112
-12	30•	22
H,-10,8		
0	174	166
2	206	181
4	227	210
-2	118	117
-4	25•	-36
-6	156	150
-8	240	228
-10	229	224
-12	142	138
H,-10,9		
0	26•	32
2	69	55
4	29•	9
-2	46	32
-4	25•	-19
-6	117	-132
-8	109	-126
-10	130	106
H,-10,10		
0	46	18
2	146	139
-2	46	35
-4	167	159
-6	217	211
-8	193	200
-10	208	193
H,-10,11		
0	27•	0
-2	68	-66
-4	89	-87
-6	28•	-37
-8	61	32
-10	125	99
H,-10,12		
-2	122	112
-4	199	189
-6	193	192
-8	172	157
H,-10,13		
-6	72	48
H,-11,0		
1	194	173
3	212	201
5	148	129
7	122	117
-9	138	131
H,-11,1		
1	90	-96
3	200	202
5	128	138
7	27•	22
-1	161	-173
-3	87	-92
-5	52	-52
-7	83	81
-9	144	144
H,-11,2		
1	200	174
3	161	144
5	166	151
7	158	142
-1	236	232
-3	110	102
-5	204	199
-7	125	112
-9	111	105
H,-11,3		
1	124	-124
3	54	-56
5	83	90
7	67	70
-1	202	-210
-3	57	45
-5	179	180
-7	138	122
-9	28•	12
H,-11,4		
1	163	139
3	224	199
5	136	118
-1	151	135
-3	248	235
-5	106	85
-7	163	154
-9	142	125
H,-11,5		
1	78	-86
3	140	-142
5	90	-91
-1	99	95
-3	92	98
-5	154	153
-7	75	63
-9	89	-112
H,-11,6		
1	228	216
3	105	83
5	132	135
-1	130	121
-3	116	110
-5	192	182
-7	153	141
-9	147	142
H,-11,7		
1	68	64
3	76	-85
-1	170	169
-3	112	112
-5	26•	-24
-7	86	-116
-9	114	-124
H,-11,8		
1	69	63
-1	180	173
-3	120	115
-5	138	133
-7	158	155
-9	215	203
H,-11,9		
1	80	71
-1	59	53
-3	40	19
-5	123	-134
-7	138	-151
-9	30•	-5
H,-11,10		
-1	79	78
-3	146	139
-5	162	146
-7	161	150
H,-12,0		
0	377	369
2	250	227
-2	246	227
-4	135	130
-6	42	-31
H,-12,1		
0	68	-60
2	28•	-4
4	75	79
6	28•	35
-2	27•	2
-4	27•	-34
-6	27•	-27
H,-12,2		
0	253	236
2	343	323
4	232	212
-2	115	110
-4	59	-57
-6	65	57
H,-12,3		
0	65	-68
2	29•	30
4	29•	-12
-2	64	-54
-4	27•	32
-6	77	66
H,-12,4		
0	71	57
2	233	204
4	282	242
-2	27•	-16
-4	65	51
-6	173	153
H,-12,5		
0	28•	32
2	29•	-37
-2	27•	-33
-4	66	53
-6	64	54
H,-12,6		
0	27•	11
-2	54	26
-4	208	200
-6	220	211
H,-12,7		
0	29•	19
-2	71	74
-4	28•	-4
-6	29•	-2
H,-13,0		
1	208	199
H,-13,1		
-1	29•	-3

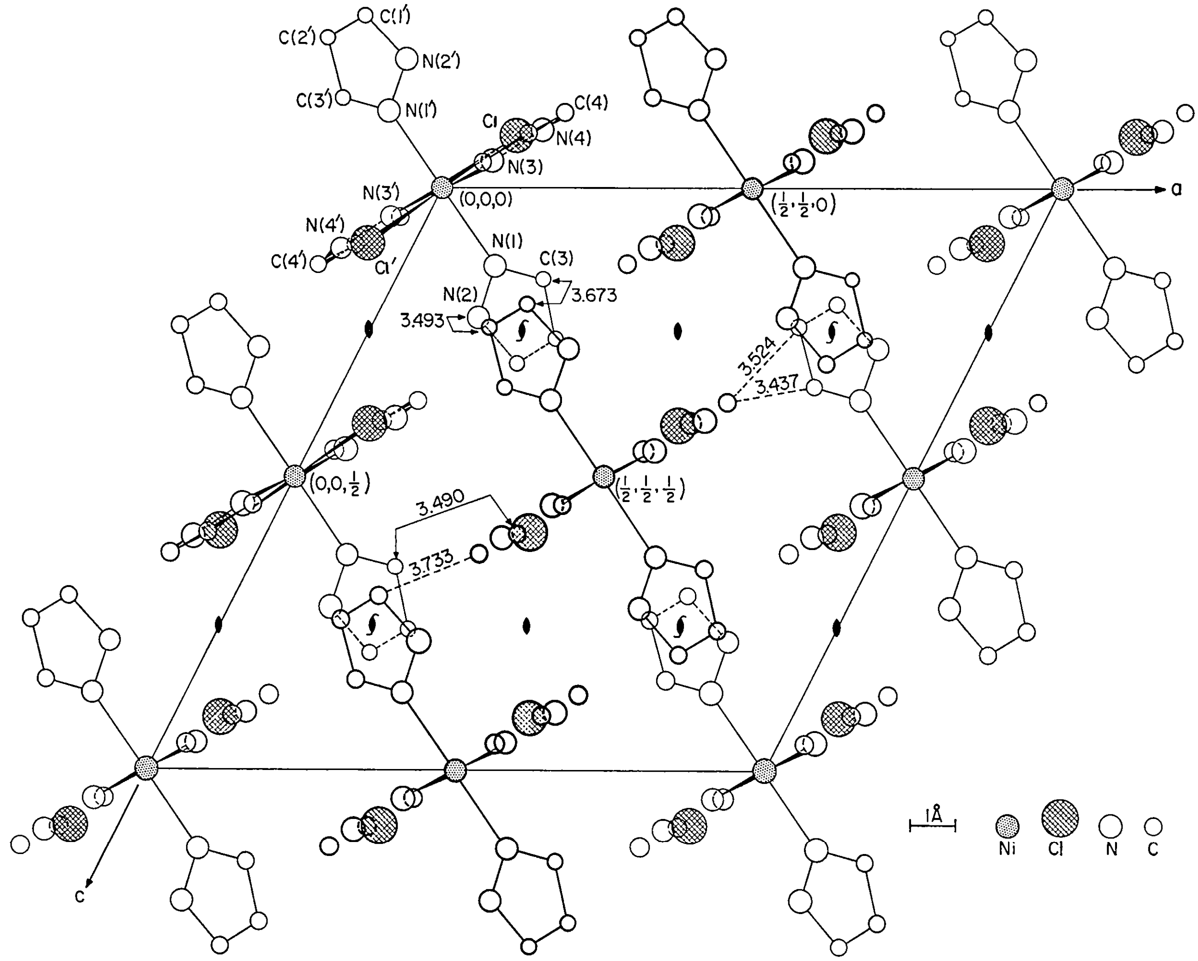

Fig. 1. Projection of the structure of $Ni(C_3H_4N_2)_4Cl_2$ along the *b* axis. The shortest intermolecular distances (Å) are indicated.

Table 5. *Bond angles*

Ring I		σ	Ring II		σ
C(3)–N(1)–N(2)	106·24°	0·24	N(4)–N(3)–C(6)	104·91°	0·31
N(1)–N(2)–C(1)	111·06	0·33	C(4)–N(4)–N(3)	111·73	0·37
N(2)–C(1)–C(2)	106·63	0·32	C(5)–C(4)–N(4)	107·40	0·51
C(1)–C(2)–C(3)	105·81	0·30	C(6)–C(5)–C(4)	104·84	0·34
C(2)–C(3)–N(1)	110·26	0·35	N(3)–C(6)–C(5)	111·13	0·38

Table 6. *Distances from the ring atoms to the least-squares planes of the pyrazole rings*

The equation of the plane in direct space is given by $PX+QY+RZ=S$. For ring I $P=7{\cdot}8403$, $Q=7{\cdot}2832$, $R=-6{\cdot}9102$, $S=0{\cdot}05461$ and for ring II $P=7{\cdot}2753$, $Q=0{\cdot}39860$, $R=7{\cdot}5473$, $S=0{\cdot}13028$.

Ring I		Ring II	
N(1)	0·0001 Å	N(3)	0·0008 Å
N(2)	0·0007	N(4)	−0·0016
C(1)	−0·0012	C(4)	0·0018
C(2)	0·0012	C(5)	−0·0012
C(3)	−0·0008	C(6)	0·0003

Table 7. *Parameters defining orientation of pyrazole rings relative to the basal plane*

The basal plane is defined by the nitrogen atoms bonded to the nickel atom. Its equation is given by $PX+QY+RZ=S$ where $P=-9{\cdot}1093$, $Q=5{\cdot}4365$, $R=10{\cdot}393$, and $S=0$.

	Ring I	Ring II
Angle between plane of ring and basal plane	91·60°	94·82°
Distance from ring centroid to basal plane	+0·08 Å	−0·15 Å
Angle between nickel-nitrogen bond and normal to ring	91·38°	93·58°

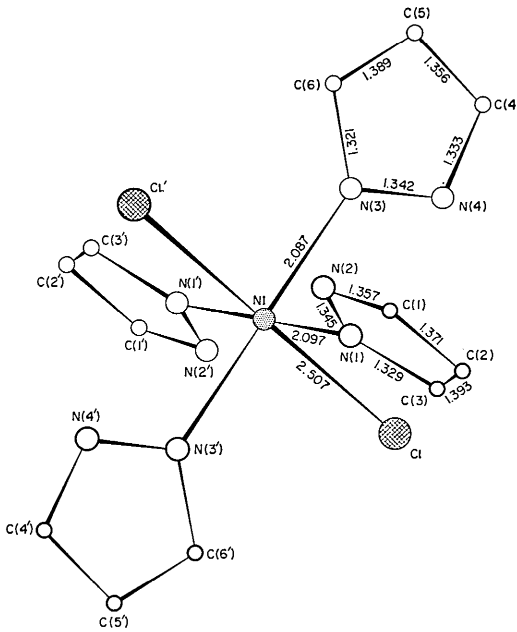

Fig. 2. Molecular structure of $Ni(C_3H_4N_2)_4Cl_2$. Unique bond distances (Å) are indicated. Average standard deviations are as follows: Ni–Cl, ±0·001; Ni–N, ±0·003; N–C, ±0·004; N–N, ±0·005; C–C, ±0·006 Å.

0·005 Å) comparable to an equi-atom structure. It is interesting, therefore, to compare the average ring bond distances for this structure with those reported for pyrazole (Ehrlich, 1960). This comparison of the pyrazole structures can only be made, however, if a reassignment is made of the hydrogen atom from one nitrogen atom to the other in Ehrlich's structure. This conclusion follows from the fact that the alternative to this reassignment would require that pyrazole coordinate to the nickel atom through the $\overset{\diagdown}{\underset{\diagup}{\text{N}}}$–H group rather than through the $\overset{\diagdown}{\underset{\diagup}{\text{N}}}$ group which contradicts the location of the hydrogen atoms in the difference map. Coordination through the $\overset{\diagdown}{\underset{\diagup}{\text{N}}}$ group is, of course, sterically more reasonable.

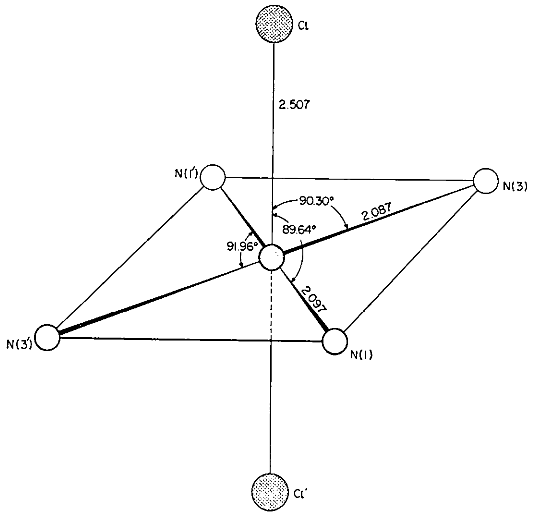

Fig. 3. Octahedral coordination about the nickel atom. Unique bond distances (Å) and angles are indicated.

The required reassignment of the hydrogen atom in Ehrlich's structure is of considerable chemical and theoretical importance and will be discussed in some detail in the chemical literature.

We would like to acknowledge that all computer calculations on this structure were performed using the X-ray 63 system of programs developed at the University of Maryland and at the University of Washington. We would also like to thank Dr George Candela for carrying out the magnetic susceptibility measurements.

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