# Crystal Structures of Complexes of Nickel Perchlorate with Substituted Pyridines. II. Tetrakis(3,4-dimethylpyridine)nickel(II) Perchlorate*

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X-ray structure analysis shows that the yellow solid $Ni(3,4\text{-dimethylpyridine})_4(ClO_4)_2$ contains the complex ion $Ni(3,4\text{-dimethylpyridine})_4^{2+}$ in which nickel exhibits square-planar coordination, in agreement with the interpretation of spectroscopic and magnetic studies [Buffagni, Vallarino & Quagliano, *Inorg. Chem.* (1964), **3**, 671]. Crystals of the compound have the Laue symmetry $4/m$; $a=b=10\cdot3277$ (14), $c=15\cdot6136$ (37) Å, $Z=2$. Intensities of 1028 independent reflections (Cu $K\alpha$ radiation, $\sin\theta/\lambda\leq0\cdot639$) were recorded with the Oak Ridge computer-controlled diffractometer and were corrected for absorption. All of the carbon and nitrogen atoms of the organic ligand except the carbon of the 3-methyl group were immediately recognizable directly as Ni–N and Ni–C peaks in a Patterson map. Coordinates for the other atoms, which were not found from the Patterson map because of disorder in the structure, were obtained from a Fourier synthesis. The Patterson map showed that the symmetry of the disordered crystal structure is either very nearly or exactly that of space group $I4/m$, which was assumed to be the appropriate one in the subsequent analysis. After full-matrix least-squares refinement, the final value of the usual discrepancy index $R(F)$ is $0\cdot071$.

The organic ligands are in twofold rotational disorder about their axes from nitrogen to 4-methyl. The symmetry of the disordered ion is, in the statistical sense, that of point group $4/m$. The planes of the ligands are perpendicular to the mirror $m$. The bonds Ni–N, which are rotated $19\cdot9°$ from coincidence with the directions of the vectors **a** and **b**, are $1\cdot897$ (3) Å long. Two of the oxygen atoms of the perchlorate ion are held on the fourfold axis $0,0,z$ by non-bonded contacts with other atoms, and their parameters are fairly well determined. The other two oxygen atoms and the chlorine atom are in fourfold disorder about the axis $0,0,z$, and their parameters are poorly determined.

## Introduction

Magnetic and spectroscopic data have been interpreted (for pertinent references see part I of this series, Madaule-Aubry & Brown, 1968) as showing that the blue compound bisperchloratotetrakis(3,5-dimethylpyridine)nickel(II) is an octahedral complex compound in which perchlorate ions are coordinated to nickel and that the yellow tetrakis(3,4-dimethylpyridine)nickel(II) perchlorate contains square-planar complex ions with no coordination by perchlorate. In part I confirmation of the interpretation for the 3,5-dimethylpyridine compound was reported from the results of X-ray crystal-structure analysis. We now report an X-ray analysis which confirms the interpretation of magnetic and spectroscopic data for the 3,4-dimethylpyridine complex compound and provides a description of the square-planar ion.

## Data

A sample of $Ni(3,4\text{-dimethylpyridine})_4(ClO_4)_2$ powder was given to us by Dr L. Vallarino of the Florida State University. Well-formed tetragonal bipyramids were

easily grown by evaporation of solvent from a solution of the compound in dichloromethane. A specimen in its natural habit, 0·5 mm in its largest dimension, was sealed inside a thin-walled glass tube for protection from the atmosphere.

From X-ray precession films the Laue group was found to be $4/m$, and the systematic absences $(h+k+l=2n+1)$ were those characteristic of space groups $I4$, $I\bar{4}$, and $I4/m$. Approximate cell parameters obtained from the precession films were refined by the method of least squares from angle data of 5 reflections (Cu $K\alpha_1$ radiation, wavelength of $1\cdot54051$ Å assumed) recorded with the Oak Ridge automatic computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) in the range 122 to $128\cdot5°$ $2\theta$. The cell parameters found are $a=b=10\cdot3277(14)$, $c=15\cdot6136(37)$ Å.* Since the volume of the cell, $1665\cdot4$ Å³, is almost exactly one fourth of the volume found for the 3,5-dimethylpyridine compound in which there are 8 formula units per cell, the number of formula units per cell in this case is 2.

Intensity data for 1028 independent reflections $(\sin\theta/\lambda\leq0\cdot639)$ were recorded with the automatic diffractometer using Cu $K\alpha$ radiation and the $\theta$–$2\theta$ step-scan method. The procedure of recording and proces-

* The numbers in parentheses, which correspond to the least-significant digits of the parameters, are the standard errors from the least-squares refinement. We use this convention for indicating standard errors throughout the paper.

sing of data was almost identical with that followed in the work on Ni(3,5-dimethylpyridine)$_4$(ClO$_4$)$_2$ described in part I. The count time for each point in a scan was 3 seconds; the count time for background at the beginning and end of a scan was 15 seconds. A nickel filter was used in recording the reflections from 0 to 133·5° $2\theta$; no filter was used for the reflections in the range 133·5 to 159·6°. Reflections 260 and 3,11,6, respectively, were used as reference reflections in these two ranges. The data of the two ranges were assigned two different scale-factor identifiers. Absorption corrections were applied ($\mu = 26\cdot9$ cm$^{-1}$).

The value 4·2 Å$^2$ for the overall isotropic temperature factor $B$ and an approximate value for the scale factor on the observations were obtained by the method of Wilson (1942).

### Solution and refinement

The nickel atoms are required by symmetry to be at the points 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ for either space group $I\bar{4}$ or space group $I4/m$, and they may be conveniently set at these points for space group $I4$. We expected to be able to locate the chlorine atoms from a Patterson synthesis; but when a Patterson map was calculated (with coefficients sharpened and modified as described by Donohue & Trueblood, 1952), we were surprised to be unable to identify a peak attributable to a vector between nickel and chlorine. However, all except one of the nitrogen and carbon atoms of the organic ligand were immediately recognized directly in the Patterson map. The configuration of the five most prominent peaks of the map, after the origin peak, described a 4-methylpyridine group with its nitrogen atom coordinated to nickel (represented on the map by the origin peak), with its axis from N to CH$_3$ lying in the mirror plane at $z = 0$, and with its plane parallel to c. No peaks were positively identified at this stage for the interactions between nickel and the carbon of the 3-methyl group or between nickel and the oxygen atoms. The absence of a prominent Ni–Cl peak indicated a high degree of orientational disorder for the perchlorate groups, and the absence of a recognizable peak for the vector Ni to 3-methyl suggested a twofold rotational disorder for each organic ligand about its axis from N to 4-methyl.

Since it was clear from the Patterson map that the symmetry of the crystal structure is either exactly or very nearly that of space group $I4/m$, this space group was assumed to be the actual one in the subsequent analysis. Structure factors were computed for the partial structure consisting of the nickel atoms and the five atoms of the 3,4-dimethylpyridine group which had been located, yielding a discrepancy index $R(F)$ of 0·38. The signs of these structure factors and the observed structure-factor magnitudes were used to compute a weighted Fourier synthesis (Woolfson, 1956), from which the carbon, C(4), of the 3-methyl group and the atoms of a poorly resolved, disordered perchlorate

group were found. Two of the oxygen atoms, O(1) and O(2), of the perchlorate ion were found on the fourfold axis $0,0,z$. The other two oxygen atoms and the chlorine atoms are in fourfold rotational disorder about this axis.

When all of the atoms except hydrogen atoms were included in the structure-factor calculations, the discrepancy index $R(F)$ first took the value 0·28, then fell on least-squares refinement with isotropic thermal parameters to 0·25, and then decreased on refinement with anisotropic thermal parameters to 0·12. Subsequently the hydrogen atoms were represented in the structure-factor calculations. Peaks representing the hydrogen atoms attached to C(3) and C(4) were located in a difference map. For the three hydrogen atoms attached to C(4) coordinates were entered, as suggested by the difference map and packing considerations, which describe a methyl group with C–H bonds 1·00 Å long and tetrahedral angles and with one hydrogen lying in the mirror plane at $z = 0$. The hydrogen atoms attached to C(5) were represented by six half-weight hydrogen atoms on a circle. Each hydrogen atom was given thermal parameters equal to those of the atom to which it is attached; neither these thermal parameters nor the coordinates were adjusted.

The final values of the usual measures of goodness-of-fit* are as follows: $R(F) = 0\cdot071$; $R(F^2) = 0\cdot112$; $R_w = 0\cdot160$; $\sigma_1 = 3\cdot52$. In the full-matrix least-squares refinement the quantity minimized was the sum $\sum w(|F_o|^2 - S^2|F_c|^2)^2$, where $S$ is the factor which scales the calculated structure-factor magnitudes $|F_c|$ to the observed magnitudes $|F_o|$ for a given group of reflections and $w$ is the weight of a reflection, calculated as the reciprocal of the variance $\sigma^2(F^2)$, which includes the same empirical variance correction described in part I. Different scale factors were used for the two groups of data recorded with different reference reflections. The scattering factors used for carbon, nitrogen, oxygen, and chlorine were the neutral-atom factors from self-consistent wave-functions as tabulated on pages 202–203 of *International Tables for X-ray Crystallography* (1962). In the early stages of refinement we used the tabulated factors in the same source for the neutral nickel atom, but in the final cycles we used the factors for Ni$^{2+}$, corrected for dispersion by a constant $\Delta f' = -3\cdot1$ (page 214, *International Tables*, 1962). The scattering factors used for the hydrogen atoms are those of Stewart, Davidson & Simpson (1965).

The observed structure-factor magnitudes $|F_o|$ and the calculated structure factors $F_c$ are listed in Table 1. Each entry $|F_o|$ has been scaled by the factor $1/S$, where $S$ is the appropriate scale factor on $F_c$ established in the refinement. For each reflection for which $|F_o|^2 \geq \sigma(F^2)$ the standard error of $|F_o|$, computed as $\sigma(F) = \sigma(F^2)/2|F_o|$, is given in the table; for each of the 58 reflections, marked $W$, for which $|F_o|^2 < \sigma(F^2)$ the quantity $\sigma(F^2)$ of $|F_o|^2$ is given. The 24 reflections of

Table 1. *Observed and calculated structure factors for* Ni(3,4-*dimethylpyridine*)$_4$(ClO$_4$)$_2$

For each reflection, identified by the indices *h* and *k* of a subheading and the running index *l*, the values of $|F_o| \times 10$ and $F_c \times 10$ are given. The standard error × 10 of $|F_o|$, calculated as $\sigma(F^2)/2|F_o|$, is given under the heading *SG*, except that for each reflection marked *W*, for which $|F_o|^2 < \sigma(F^2)$, the standard error $\sigma(F^2) \times 10$ of $|F_o|^2$ is given instead. The 24 reflections marked *X* are the reflections of highest intensity, which were excluded from the final refinement as having $|F_o|$ values in error because of extinction.

| L | OBS | CAL | SG |
|---|---|---|---|
| *** 0 0 L *** | | | |
| 2X | 855 | 1209 | 13 |
| 4X | 1095 | 1382 | 16 |
| 6 | 138 | 165 | 2 |
| 8 | 315 | 268 | 5 |
| 10 | 511 | 489 | 8 |
| 12 | 280 | 246 | 4 |
| 14 | 540 | 571 | 8 |
| 16 | 21 | 21 | 8 |
| 18 | 80 | 79 | 2 |
| *** 0 1 L *** | | | |
| 1X | 479 | 556 | 7 |
| 3X | 902 | 1131 | 14 |
| 5 | 133 | -73 | 2 |
| 7 | 436 | 432 | 7 |
| 9 | 51 | -66 | 3 |
| 11 | 464 | 467 | 7 |
| 13 | 111 | 108 | 3 |
| 15 | 86 | 95 | 3 |
| 17 | 82 | 79 | 2 |
| 19 | 13 | -10 | 5 |
| *** 0 2 L *** | | | |
| 0X | 920 | 1180 | 14 |
| 2 | 436 | -474 | 7 |
| 4 | 601 | 633 | 9 |
| 6 | 462 | 439 | 7 |
| 8 | 431 | 386 | 7 |
| 10 | 285 | 273 | 4 |
| 12 | 130 | -132 | 3 |
| 14 | 203 | 205 | 3 |
| 16 | 37 | -39 | 5 |
| 18 | 67 | 73 | 2 |
| *** 0 3 L *** | | | |
| 1 | 428 | -442 | 6 |
| 3 | 262 | 280 | 4 |
| 5 | 74 | 80 | 2 |
| 7 | 65 | -65 | 2 |
| 9 | 48 | 57 | 3 |
| 11 | 136 | 133 | 3 |
| 13W | 16 | 4 | 36 |
| 15W | 17 | -20 | 33 |
| 17 | 39 | 44 | 3 |
| 19W | 0 | -5 | 11 |
| *** 0 4 L *** | | | |
| 0 | 29 | 39 | 3 |
| 2 | 104 | -102 | 2 |
| 4 | 323 | 342 | 5 |
| 6 | 344 | 332 | 5 |
| 8 | 304 | 284 | 5 |
| 10 | 176 | 161 | 3 |
| 12 | 113 | -109 | 3 |
| 14 | 88 | 79 | 3 |
| 16W | 0 | -8 | 27 |
| 18 | 39 | 36 | 2 |
| *** 0 5 L *** | | | |
| 1 | 450 | 462 | 7 |
| 3 | 445 | 492 | 7 |
| 5 | 482 | 536 | 7 |
| 7 | 359 | 356 | 5 |
| 9 | 193 | 195 | 3 |
| 11 | 172 | 168 | 3 |
| 13 | 71 | 82 | 3 |
| 15W | 15 | 31 | 29 |
| 17 | 48 | 52 | 2 |
| *** 0 6 L *** | | | |
| 0 | 223 | 221 | 3 |
| 2 | 41 | 32 | 3 |
| 4 | 216 | 234 | 3 |
| 6 | 239 | 253 | 4 |
| 8 | 237 | 247 | 4 |
| 10 | 151 | 137 | 3 |
| 12W | 16 | 13 | 34 |
| 14 | 44 | 41 | 3 |
| 16W | 4 | 19 | 20 |
| *** 0 7 L *** | | | |
| 1 | 130 | 150 | 2 |
| 3 | 169 | 194 | 3 |
| 5 | 344 | 370 | 5 |
| 7 | 246 | 239 | 4 |
| 9 | 161 | 166 | 3 |
| 11 | 61 | 51 | 3 |
| 13 | 30 | 26 | 5 |
| 15 | 22 | -3 | 4 |
| *** 0 8 L *** | | | |
| 0 | 83 | 88 | 2 |
| 2 | 93 | 106 | 2 |
| 4 | 97 | -87 | 3 |
| 6 | 117 | -131 | 3 |
| 8 | 106 | -97 | 3 |
| 10 | 24 | -13 | 6 |
| 12 | 41 | 49 | 4 |
| 14 | 19 | 24 | 6 |
| *** 0 9 L *** | | | |
| 1 | 153 | 158 | 3 |
| 3 | 65 | 72 | 3 |
| 5 | 55 | 49 | 3 |
| 7 | 68 | -76 | 3 |
| 9 | 50 | 56 | 3 |
| 11 | 24 | 25 | 5 |
| 13 | 52 | 48 | 2 |
| *** 0 10 L *** | | | |
| 0 | 56 | -65 | 3 |
| 2 | 33 | 23 | 5 |
| 4 | 35 | 40 | 5 |
| 6 | 101 | 99 | 2 |
| 8 | 66 | 68 | 3 |
| 10 | 16 | 7 | 7 |
| 12W | 6 | 6 | 16 |
| *** 0 11 L *** | | | |
| 1 | 103 | 107 | 2 |
| 3 | 86 | 92 | 2 |
| 5 | 99 | 97 | 2 |
| 7 | 53 | 45 | 2 |
| 9 | 73 | 68 | 2 |
| *** 0 12 L *** | | | |
| 0 | 124 | 133 | 2 |
| 2 | 120 | 129 | 2 |
| 4 | 96 | 93 | 2 |
| 6 | 97 | 95 | 2 |
| 8 | 75 | 77 | 2 |
| *** 0 13 L *** | | | |
| 1 | 89 | 89 | 2 |
| 3 | 66 | 65 | 2 |
| *** 1 0 L *** | | | |
| 1X | 524 | 556 | 8 |
| 3X | 934 | 1131 | 14 |
| 5 | 138 | -73 | 2 |
| 7 | 443 | 432 | 7 |
| 9 | 49 | -66 | 3 |
| 11 | 465 | 467 | 7 |
| 13 | 111 | 108 | 3 |
| 15 | 88 | 95 | 3 |
| 17 | 82 | 79 | 2 |
| 19 | 20 | -10 | 5 |
| *** 1 1 L *** | | | |
| 0X | 906 | 1203 | 14 |
| 2X | 572 | -674 | 9 |
| 4X | 789 | 849 | 12 |
| 6 | 179 | 159 | 3 |
| 8 | 474 | 419 | 7 |
| 10 | 329 | 309 | 5 |
| 12 | 163 | -163 | 3 |
| 14 | 246 | 249 | 4 |
| 16 | 38 | -43 | 4 |
| 18 | 74 | 81 | 2 |
| *** 1 2 L *** | | | |
| 1X | 588 | -639 | 9 |
| 3X | 685 | 822 | 10 |
| 5X | 781 | 860 | 12 |
| 7 | 788 | 783 | 12 |
| 9 | 253 | 229 | 4 |
| 11 | 154 | 151 | 3 |
| 13 | 107 | -109 | 3 |
| 15 | 54 | -62 | 3 |
| 17 | 60 | 67 | 3 |
| 19 | 18 | 30 | 3 |
| *** 1 3 L *** | | | |
| 0X | 675 | 668 | 10 |
| 2 | 387 | -373 | 6 |
| 4 | 188 | 200 | 3 |
| 6 | 407 | 418 | 6 |
| 8 | 225 | 220 | 4 |
| 10 | 145 | 157 | 3 |
| 12 | 76 | -87 | 3 |
| 14 | 104 | 105 | 3 |
| 16 | 45 | -35 | 3 |
| 18 | 45 | 42 | 2 |
| *** 1 4 L *** | | | |
| 1 | 23 | 28 | 3 |
| 3 | 199 | 231 | 3 |
| 5 | 121 | 128 | 2 |
| 7 | 46 | -50 | 3 |
| 9W | 10 | 36 | 32 |
| 11 | 114 | 114 | 3 |
| 13 | 36 | 31 | 5 |
| 15W | 0 | -10 | 31 |
| 17 | 20 | 22 | 5 |
| *** 1 5 L *** | | | |
| 0 | 669 | 709 | 10 |
| 2 | 43 | 55 | 2 |
| 4 | 122 | 136 | 2 |
| 6 | 80 | 86 | 2 |
| 8 | 82 | 84 | 2 |
| 10 | 81 | 88 | 3 |
| 12 | 43 | 49 | 4 |
| 14 | 109 | 113 | 2 |
| 16 | 20 | 25 | 6 |
| 18 | 19 | 14 | 3 |
| *** 1 6 L *** | | | |
| 1 | 282 | 307 | 4 |
| 3 | 278 | 307 | 4 |
| 5 | 102 | 105 | 2 |
| 7 | 23 | -17 | 7 |
| 9 | 99 | 92 | 3 |
| 11 | 129 | 121 | 3 |
| 13 | 73 | 80 | 3 |
| 15 | 35 | 33 | 4 |
| 17 | 12 | 18 | 5 |
| *** 1 7 L *** | | | |
| 0 | 25 | 11 | 6 |
| 2 | 76 | 80 | 2 |
| 4 | 162 | 179 | 3 |
| 6 | 231 | 247 | 4 |
| 8 | 186 | 203 | 3 |
| 10 | 93 | 91 | 3 |
| 12W | 12 | 6 | 31 |
| 14 | 21 | 1 | 6 |
| 16 | 23 | 22 | 3 |
| *** 1 8 L *** | | | |
| 1 | 120 | 122 | 2 |
| 3 | 87 | 90 | 2 |
| 5 | 161 | 162 | 3 |
| 7W | 0 | -17 | 37 |
| 9 | 79 | 83 | 3 |
| 11W | 11 | 12 | 31 |
| 13 | 45 | 50 | 3 |
| 15 | 25 | 19 | 2 |
| *** 1 9 L *** | | | |
| 0 | 151 | 154 | 3 |
| 2 | 197 | 211 | 3 |
| 4 | 30 | -15 | 6 |
| 6 | 21 | -37 | 8 |
| 8 | 25 | -22 | 6 |
| 10 | 28 | 18 | 5 |
| 12 | 73 | 78 | 2 |
| 14 | 41 | 36 | 2 |
| *** 1 10 L *** | | | |
| 1 | 135 | 136 | 3 |
| 3 | 87 | 88 | 3 |
| 5 | 180 | 180 | 3 |
| 7 | 91 | 91 | 2 |
| 9 | 98 | 102 | 2 |
| 11 | 48 | 37 | 2 |
| *** 1 11 L *** | | | |
| 0 | 133 | 143 | 3 |
| 2 | 161 | 168 | 3 |
| 4 | 114 | 115 | 2 |
| 6 | 104 | 104 | 2 |
| 8 | 85 | 83 | 2 |
| 10 | 54 | 48 | 2 |
| *** 1 12 L *** | | | |
| 1 | 139 | 149 | 2 |
| 3 | 103 | 98 | 2 |
| 5 | 91 | 85 | 2 |
| 7 | 58 | 55 | 2 |
| *** 1 13 L *** | | | |
| 0 | 60 | 61 | 2 |
| 2 | 72 | 73 | 2 |
| *** 2 0 L *** | | | |
| 0X | 893 | 1180 | 13 |
| 2X | 502 | -474 | 8 |
| 4X | 666 | 633 | 10 |
| 6 | 489 | 439 | 7 |
| 8 | 443 | 386 | 7 |
| 10 | 285 | 273 | 4 |
| 12 | 131 | -132 | 3 |
| 14 | 203 | 205 | 3 |
| 16 | 45 | -39 | 4 |
| 18 | 65 | 73 | 2 |
| *** 2 1 L *** | | | |
| 1X | 965 | 1307 | 14 |
| 3X | 656 | 668 | 10 |
| 5 | 388 | 365 | 6 |
| 7 | 331 | 274 | 5 |
| 9 | 28 | 9 | 5 |
| 11 | 399 | 376 | 6 |
| 13 | 197 | 182 | 3 |
| 15 | 49 | 62 | 4 |
| 17 | 74 | 73 | 2 |
| 19 | 12 | -9 | 5 |
| *** 2 2 L *** | | | |
| 0 | 83 | 78 | 2 |
| 2 | 569 | -624 | 9 |
| 4 | 163 | 146 | 3 |
| 6 | 158 | 156 | 3 |
| 8 | 165 | 163 | 3 |
| 10 | 173 | 176 | 3 |
| 12 | 162 | -160 | 3 |
| 14 | 120 | 117 | 3 |
| 16 | 46 | -40 | 4 |
| 18 | 42 | 43 | 3 |
| *** 2 3 L *** | | | |
| 1 | 33 | 40 | 2 |
| 3 | 206 | 215 | 3 |
| 5 | 234 | 211 | 4 |
| 7 | 20 | -25 | 7 |
| 9 | 25 | 33 | 6 |
| 11 | 138 | 118 | 3 |
| 13 | 36 | 24 | 5 |
| 15W | 12 | -26 | 33 |
| 17 | 24 | 30 | 5 |
| 19 | 10 | -1 | 4 |
| *** 2 4 L *** | | | |
| 0 | 403 | 363 | 6 |
| 2 | 36 | -3 | 3 |
| 4 | 101 | 121 | 2 |
| 6 | 258 | -222 | 4 |
| 8 | 52 | -12 | 3 |
| 10 | 77 | 86 | 3 |
| 12 | 39 | -31 | 5 |
| 14 | 96 | 84 | 3 |
| 16W | 0 | -9 | 27 |
| 18W | 8 | -7 | 17 |
| *** 2 5 L *** | | | |
| 1 | 83 | 70 | 2 |
| 3 | 248 | 271 | 4 |
| 5 | 137 | 152 | 2 |
| 7 | 67 | 68 | 3 |
| 9 | 57 | 72 | 3 |
| 11 | 97 | 101 | 3 |
| 13 | 50 | 51 | 4 |
| 15 | 37 | 29 | 4 |
| 17 | 19 | 24 | 4 |
| *** 2 6 L *** | | | |
| 0 | 643 | 686 | 10 |
| 2 | 308 | 327 | 5 |
| 4 | 256 | 269 | 4 |
| 6 | 181 | 186 | 3 |
| 8 | 149 | 152 | 3 |
| 10 | 141 | 128 | 3 |
| 12 | 95 | 101 | 3 |
| 14 | 100 | 112 | 2 |
| 16 | 54 | 56 | 2 |
| *** 2 7 L *** | | | |
| 1 | 168 | 176 | 3 |
| 3 | 176 | 186 | 3 |
| 5 | 259 | 264 | 4 |
| 7 | 151 | 156 | 3 |
| 9 | 179 | 180 | 3 |
| 11 | 74 | 68 | 3 |
| 13 | 73 | 75 | 2 |
| 15 | 25 | 25 | 4 |
| *** 2 8 L *** | | | |
| 0 | 305 | 324 | 5 |
| 2 | 343 | 358 | 5 |
| 4 | 214 | 218 | 3 |
| 6 | 306 | 318 | 5 |
| 8 | 183 | 180 | 3 |
| 10 | 111 | 100 | 3 |
| 12 | 96 | 94 | 2 |
| 14 | 45 | 42 | 2 |
| *** 2 9 L *** | | | |
| 1 | 233 | 233 | 4 |
| 3 | 79 | 73 | 3 |
| 5W | 17 | 13 | 35 |
| 7 | 138 | -137 | 3 |
| 9 | 35 | 45 | 5 |
| 11 | 39 | 41 | 3 |
| 13 | 81 | 91 | 2 |
| *** 2 10 L *** | | | |
| 0 | 118 | 116 | 3 |
| 2 | 163 | 163 | 3 |
| 4 | 72 | 69 | 3 |
| 6 | 91 | 86 | 2 |
| 8 | 79 | 79 | 2 |
| 10 | 51 | 50 | 2 |
| 12 | 58 | 64 | 2 |
| *** 2 11 L *** | | | |
| 1W | 8 | -0 | 29 |
| 3 | 44 | 44 | 3 |
| 5 | 124 | 125 | 2 |
| 7 | 87 | 86 | 2 |
| 9 | 81 | 81 | 2 |
| *** 2 12 L *** | | | |
| 0 | 72 | 71 | 2 |
| 2 | 96 | 101 | 2 |
| 4 | 104 | 103 | 2 |
| 6 | 124 | 118 | 2 |
| *** 2 13 L *** | | | |
| 1 | 81 | 85 | 2 |
| *** 3 0 L *** | | | |
| 1 | 484 | -442 | 7 |
| 3 | 308 | 280 | 5 |
| 5 | 82 | 80 | 2 |
| 7 | 63 | -65 | 2 |
| 9 | 45 | 57 | 3 |
| 11 | 142 | 133 | 3 |
| 13W | 0 | 4 | 37 |
| 15 | 20 | -20 | 9 |
| 17 | 33 | 44 | 4 |
| 19W | 8 | -5 | 15 |
| *** 3 1 L *** | | | |
| 0X | 1401 | 2031 | 21 |
| 2X | 755 | 824 | 11 |
| 4 | 368 | 349 | 6 |
| 6 | 20 | 30 | 5 |
| 8W | 8 | 43 | 27 |
| 10 | 302 | 284 | 5 |
| 12 | 80 | 81 | 3 |
| 14 | 288 | 284 | 5 |
| 16 | 29 | 17 | 5 |
| 18 | 27 | 22 | 3 |
| *** 3 2 L *** | | | |
| 1 | 224 | -101 | 3 |
| 3 | 411 | 449 | 6 |
| 5 | 149 | 145 | 2 |
| 7 | 42 | -17 | 3 |
| 9 | 127 | 125 | 2 |
| 11 | 131 | 128 | 3 |
| 13 | 62 | 61 | 3 |
| 15W | 15 | 5 | 33 |
| 17 | 44 | 48 | 3 |
| 19 | 19 | -6 | 2 |
| *** 3 3 L *** | | | |
| 0 | 235 | 249 | 4 |
| 2 | 84 | -79 | 2 |
| 4 | 301 | 314 | 5 |
| 6 | 424 | 405 | 6 |
| 8 | 307 | 292 | 5 |
| 10 | 156 | 137 | 3 |
| 12 | 75 | -73 | 3 |
| 14 | 86 | 74 | 3 |
| 16W | 15 | -0 | 26 |
| 18 | 32 | 33 | 2 |
| *** 3 4 L *** | | | |
| 1 | 241 | 215 | 4 |
| 3 | 134 | 140 | 2 |
| 5 | 105 | 115 | 2 |
| 7 | 23 | 3 | 6 |
| 9W | 16 | 21 | 33 |
| 11 | 129 | 128 | 3 |
| 13 | 80 | 83 | 3 |
| 15 | 19 | 28 | 8 |
| 17 | 26 | 28 | 3 |
| *** 3 5 L *** | | | |
| 0 | 706 | 726 | 11 |
| 2 | 256 | 267 | 4 |
| 4 | 269 | 270 | 4 |
| 6 | 148 | 135 | 3 |
| 8 | 145 | 143 | 3 |
| 10 | 121 | 105 | 3 |
| 12 | 77 | 79 | 3 |
| 14 | 114 | 110 | 2 |
| 16 | 40 | 42 | 3 |
| *** 3 6 L *** | | | |
| 1 | 613 | 632 | 9 |
| 3 | 388 | 397 | 6 |
| 5 | 280 | 299 | 4 |
| 7 | 146 | 161 | 3 |
| 9 | 151 | 149 | 3 |
| 11 | 170 | 174 | 3 |
| 13 | 149 | 161 | 3 |
| 15 | 75 | 80 | 2 |
| 17 | 36 | 44 | 1 |
| *** 3 7 L *** | | | |
| 0 | 285 | 311 | 4 |
| 2 | 298 | 305 | 5 |
| 4 | 161 | 162 | 3 |
| 6 | 149 | 159 | 3 |
| 8 | 134 | 140 | 3 |
| 10 | 149 | 137 | 3 |
| 12 | 84 | 91 | 2 |
| 14 | 58 | 61 | 2 |
| 16 | 45 | 48 | 1 |
| *** 3 8 L *** | | | |
| 1 | 76 | 82 | 3 |
| 3 | 138 | 151 | 3 |
| 5 | 304 | 315 | 5 |
| 7 | 182 | 191 | 3 |
| 9 | 212 | 213 | 3 |
| 11 | 39 | 32 | 4 |
| 13 | 26 | 35 | 4 |
| 15W | 0 | 2 | 9 |
| *** 3 9 L *** | | | |
| 0 | 22 | 1 | 8 |
| 2 | 111 | 116 | 2 |
| 4 | 44 | 38 | 4 |
| 6 | 87 | 86 | 3 |
| 8 | 67 | 61 | 3 |
| 10 | 44 | 33 | 3 |
| 12 | 39 | 40 | 3 |
| *** 3 10 L *** | | | |
| 1 | 123 | 124 | 3 |
| 3 | 100 | 107 | 2 |
| 5 | 156 | 156 | 3 |
| 7 | 87 | 77 | 2 |
| 9 | 99 | 107 | 2 |
| 11 | 40 | 34 | 2 |
| *** 3 11 L *** | | | |
| 0W | 0 | 2 | 28 |
| 2 | 59 | 62 | 3 |
| 4 | 116 | 121 | 2 |
| 6 | 178 | 178 | 3 |
| 8 | 127 | 129 | 2 |
| *** 3 12 L *** | | | |
| 1 | 77 | 78 | 2 |
| 3 | 79 | 76 | 2 |
| 5 | 87 | 89 | 2 |
| *** 4 0 L *** | | | |
| 0 | 24 | 39 | 4 |
| 2 | 122 | -102 | 2 |
| 4 | 384 | 342 | 6 |
| 6 | 389 | 332 | 6 |
| 8 | 326 | 284 | 5 |
| 10 | 184 | 161 | 3 |
| 12 | 119 | -109 | 3 |
| 14 | 96 | 79 | 3 |
| 16W | 5 | -8 | 29 |
| 18 | 35 | 36 | 3 |
| *** 4 1 L *** | | | |
| 1X | 690 | 625 | 10 |
| 3 | 430 | 409 | 6 |
| 5 | 281 | 266 | 4 |
| 7 | 115 | 117 | 2 |
| 9 | 110 | 117 | 2 |
| 11 | 217 | 218 | 4 |
| 13 | 181 | 186 | 3 |
| 15 | 65 | 67 | 3 |
| 17 | 62 | 65 | 2 |
| *** 4 2 L *** | | | |
| 0X | 1285 | 1509 | 19 |
| 2 | 622 | 607 | 9 |
| 4 | 308 | 299 | 5 |
| 6 | 353 | 309 | 5 |
| 8 | 163 | 147 | 3 |
| 10 | 263 | 229 | 4 |
| 12 | 128 | 131 | 3 |
| 14 | 228 | 230 | 4 |
| 16 | 52 | 58 | 3 |
| 18 | 35 | 31 | 2 |
| *** 4 3 L *** | | | |
| 1 | 373 | 336 | 6 |
| 3 | 451 | 453 | 7 |
| 5 | 458 | 481 | 7 |
| 7 | 309 | 287 | 5 |
| 9 | 211 | 202 | 3 |
| 11 | 145 | 140 | 3 |
| 13 | 63 | 72 | 3 |
| 15W | 16 | 25 | 30 |
| 17 | 48 | 51 | 2 |
| *** 4 4 L *** | | | |
| 0 | 721 | 709 | 11 |
| 2 | 257 | 260 | 4 |
| 4 | 249 | 263 | 4 |
| 6 | 177 | 179 | 3 |
| 8 | 167 | 168 | 3 |
| 10 | 167 | 143 | 3 |
| 12 | 66 | 74 | 3 |
| 14 | 97 | 97 | 2 |
| 16 | 26 | 32 | 4 |
| *** 4 5 L *** | | | |
| 1 | 110 | 113 | 2 |
| 3 | 205 | 222 | 3 |
| 5 | 79 | 100 | 3 |
| 7W | 0 | -2 | 35 |
| 9 | 111 | 113 | 3 |
| 11 | 88 | 95 | 3 |
| 13 | 46 | 49 | 4 |
| 15 | 25 | 22 | 5 |
| 17 | 15 | 12 | 3 |
| *** 4 6 L *** | | | |
| 0 | 171 | 167 | 3 |
| 2 | 157 | 144 | 3 |
| 4 | 172 | 187 | 3 |
| 6 | 233 | 278 | 4 |
| 8 | 194 | 200 | 3 |
| 10 | 123 | 110 | 3 |
| 12 | 43 | 45 | 4 |
| 14 | 42 | 46 | 3 |
| 16 | 35 | 39 | 2 |
| *** 4 7 L *** | | | |
| 1 | 228 | 248 | 4 |
| 3 | 245 | 260 | 4 |
| 5 | 341 | 346 | 5 |
| 7 | 210 | 219 | 3 |
| 9 | 229 | 220 | 4 |
| 11 | 84 | 79 | 3 |
| 13 | 67 | 68 | 2 |
| 15 | 29 | 23 | 2 |
| *** 4 8 L *** | | | |
| 0W | 12 | -7 | 34 |
| 2 | 146 | 142 | 3 |
| 4 | 202 | 215 | 3 |
| 6 | 362 | 377 | 6 |
| 8 | 255 | 262 | 4 |
| 10 | 107 | 104 | 2 |
| 12 | 35 | 26 | 3 |
| 14 | 11 | -14 | 5 |
| *** 4 9 L *** | | | |
| 1 | 133 | 141 | 3 |
| 3 | 121 | 126 | 3 |
| 5 | 221 | 226 | 4 |
| 7 | 107 | 109 | 2 |
| 9 | 106 | 106 | 2 |
| 11 | 33 | 19 | 3 |
| 13 | 28 | 33 | 2 |
| *** 4 10 L *** | | | |
| 0 | 75 | 73 | 3 |
| 2 | 77 | 80 | 3 |
| 4 | 51 | -47 | 3 |
| 6 | 82 | -88 | 2 |
| 8 | 63 | -63 | 2 |
| 10 | 21 | -14 | 4 |
| *** 4 11 L *** | | | |
| 1 | 53 | 54 | 3 |
| 3 | 30 | 20 | 4 |
| 5 | 16 | 13 | 7 |
| 7 | 25 | -25 | 4 |
| 9W | 10 | 14 | 13 |
| *** 4 12 L *** | | | |
| 0 | 47 | 46 | 2 |
| 2 | 57 | 55 | 2 |
| 4 | 15 | 17 | 5 |
| *** 5 0 L *** | | | |
| 1 | 488 | 462 | 7 |
| 3 | 531 | 492 | 8 |
| 5 | 565 | 536 | 9 |
| 7 | 402 | 356 | 6 |
| 9 | 204 | 195 | 3 |
| 11 | 181 | 168 | 3 |
| 13 | 75 | 82 | 3 |
| 15 | 26 | 31 | 6 |
| 17 | 44 | 52 | 3 |
| *** 5 1 L *** | | | |
| 0 | 813 | 862 | 12 |
| 2 | 405 | 382 | 6 |
| 4 | 355 | 338 | 5 |
| 6 | 242 | 218 | 4 |
| 8 | 205 | 185 | 3 |
| 10 | 244 | 209 | 4 |
| 12 | 55 | 71 | 4 |
| 14 | 144 | 152 | 3 |
| 16 | 40 | 47 | 3 |
| 18 | 28 | 26 | 2 |
| *** 5 2 L *** | | | |
| 1X | 913 | 908 | 14 |
| 3 | 607 | 610 | 9 |
| 5 | 285 | 275 | 4 |
| 7 | 112 | 114 | 2 |
| 9 | 228 | 202 | 4 |
| 11 | 274 | 255 | 4 |
| 13 | 201 | 213 | 3 |
| 15 | 96 | 96 | 2 |
| 17 | 44 | 50 | 2 |
| *** 5 3 L *** | | | |
| 0 | 94 | -78 | 2 |
| 2 | 97 | -93 | 2 |
| 4 | 192 | 195 | 3 |
| 6 | 226 | 225 | 4 |
| 8 | 255 | 255 | 4 |
| 10 | 158 | 138 | 3 |
| 12 | 44 | -31 | 4 |
| 14 | 40 | 33 | 4 |
| 16 | 23 | 18 | 5 |
| *** 5 4 L *** | | | |
| 1 | 18 | 6 | 7 |
| 3 | 231 | 249 | 4 |
| 5 | 433 | 435 | 7 |
| 7 | 377 | 351 | 6 |
| 9 | 239 | 224 | 4 |
| 11 | 77 | 56 | 3 |
| 13 | 23 | -6 | 7 |
| 15W | 0 | -15 | 25 |
| 17 | 20 | 28 | 4 |
| *** 5 5 L *** | | | |
| 0 | 172 | 158 | 3 |
| 2 | 117 | 114 | 2 |
| 4 | 191 | 211 | 3 |
| 6 | 271 | 278 | 4 |
| 8 | 191 | 208 | 3 |
| 10 | 98 | 92 | 3 |
| 12W | 10 | 22 | 33 |
| 14W | 12 | 12 | 25 |
| 16 | 19 | 19 | 4 |
| *** 5 6 L *** | | | |
| 1 | 178 | 178 | 3 |
| 3 | 190 | 207 | 3 |
| 5 | 316 | 326 | 5 |
| 7 | 189 | 197 | 3 |
| 9 | 148 | 149 | 3 |
| 11 | 52 | 50 | 3 |
| 13 | 41 | 43 | 3 |
| 15 | 25 | 17 | 4 |
| *** 5 7 L *** | | | |
| 0 | 269 | 290 | 4 |
| 2 | 269 | 271 | 4 |
| 4 | 125 | 132 | 3 |
| 6 | 144 | 148 | 3 |
| 8 | 65 | 73 | 3 |
| 10 | 72 | 71 | 3 |
| 12 | 77 | 86 | 2 |
| 14 | 47 | 57 | 2 |
| *** 5 8 L *** | | | |
| 1 | 67 | 71 | 3 |
| 3 | 29 | 36 | 6 |
| 5 | 43 | 27 | 4 |
| 7 | 61 | -60 | 3 |
| 9 | 52 | 48 | 3 |
| 11 | 24 | 19 | 5 |
| 13 | 44 | 45 | 2 |
| *** 5 9 L *** | | | |
| 0 | 104 | 96 | 2 |
| 2 | 135 | 137 | 3 |
| 4 | 54 | 58 | 3 |
| 6 | 43 | 42 | 4 |
| 8 | 41 | 32 | 3 |
| 10 | 32 | 28 | 3 |
| 12 | 47 | 44 | 2 |
| *** 5 10 L *** | | | |
| 1 | 108 | 108 | 2 |
| 3W | 0 | 17 | 29 |
| 5 | 56 | -65 | 3 |
| 7 | 109 | -119 | 2 |
| 9 | 21 | -19 | 5 |
| *** 5 11 L *** | | | |
| 0 | 95 | 97 | 2 |
| 2 | 89 | 94 | 2 |
| 4 | 48 | 41 | 2 |
| 6 | 35 | 27 | 3 |
| *** 5 12 L *** | | | |
| 1W | 0 | -2 | 15 |
| 3 | 28 | 23 | 2 |
| *** 6 0 L *** | | | |
| 0 | 237 | 221 | 4 |
| 2 | 64 | 32 | 2 |
| 4 | 262 | 234 | 4 |
| 6 | 277 | 253 | 4 |
| 8 | 259 | 247 | 4 |
| 10 | 160 | 137 | 3 |
| 12W | 3 | 13 | 37 |
| 14 | 46 | 41 | 4 |
| 16 | 18 | 19 | 6 |
| *** 6 1 L *** | | | |
| 1 | 230 | -173 | 4 |
| 3 | 218 | 228 | 3 |
| 5 | 389 | 368 | 6 |
| 7 | 335 | 304 | 5 |
| 9 | 253 | 230 | 4 |
| 11 | 73 | 56 | 3 |
| 13 | 30 | -14 | 6 |
| 15W | 13 | -11 | 26 |
| 17 | 21 | 30 | 4 |
| *** 6 2 L *** | | | |
| 0 | 743 | 714 | 11 |
| 2 | 459 | 429 | 7 |
| 4 | 419 | 400 | 6 |
| 6 | 432 | 418 | 7 |
| 8 | 323 | 320 | 5 |
| 10 | 206 | 188 | 3 |
| 12 | 111 | 115 | 3 |
| 14 | 101 | 106 | 2 |
| 16 | 46 | 53 | 3 |
| *** 6 3 L *** | | | |
| 1 | 277 | 277 | 4 |
| 3 | 309 | 317 | 5 |
| 5 | 432 | 434 | 7 |
| 7 | 297 | 294 | 5 |
| 9 | 198 | 197 | 3 |
| 11 | 114 | 101 | 3 |
| 13 | 63 | 58 | 3 |
| 15 | 35 | 28 | 3 |
| 17 | 32 | 39 | 2 |
| *** 6 4 L *** | | | |
| 0 | 81 | 78 | 2 |
| 2 | 73 | 75 | 3 |
| 4 | 221 | 227 | 4 |
| 6 | 317 | 320 | 5 |
| 8 | 214 | 205 | 4 |
| 10 | 65 | 68 | 3 |
| 12W | 0 | -0 | 33 |
| 14W | 0 | -0 | 25 |
| 16 | 27 | 26 | 3 |
| *** 6 5 L *** | | | |
| 1 | 103 | 99 | 2 |
| 3W | 8 | 19 | 33 |
| 5W | 16 | -17 | 35 |
| 7 | 137 | -144 | 3 |
| 9W | 0 | -10 | 36 |
| 11 | 31 | 28 | 5 |
| 13 | 41 | 48 | 3 |
| 15 | 25 | 20 | 3 |
| *** 6 6 L *** | | | |
| 0 | 115 | 110 | 3 |
| 2 | 136 | 136 | 3 |
| 4 | 52 | -49 | 4 |
| 6 | 129 | -145 | 3 |
| 8 | 91 | -92 | 3 |
| 10W | 9 | 6 | 31 |
| 12 | 38 | 44 | 4 |
| 14 | 41 | 38 | 2 |
| *** 6 7 L *** | | | |
| 1 | 264 | 258 | 4 |
| 3 | 135 | 143 | 3 |
| 5 | 53 | 44 | 4 |
| 7 | 63 | -58 | 3 |
| 9 | 56 | 54 | 3 |
| 11 | 60 | 63 | 2 |
| 13 | 84 | 90 | 2 |
| *** 6 8 L *** | | | |
| 0 | 185 | 194 | 3 |
| 2 | 189 | 195 | 3 |
| 4 | 76 | 81 | 3 |
| 6 | 66 | 58 | 3 |
| 8 | 52 | 59 | 3 |
| 10 | 63 | 64 | 2 |
| 12 | 69 | 70 | 2 |
| *** 6 9 L *** | | | |
| 1 | 51 | 50 | 3 |
| 3 | 76 | 76 | 2 |
| 5 | 159 | 164 | 3 |
| 7 | 126 | 132 | 2 |
| 11 | 32 | 27 | 2 |
| *** 6 10 L *** | | | |
| 0W | 12 | 14 | 25 |
| 2 | 24 | 28 | 5 |
| 4 | 34 | 32 | 4 |
| 6 | 56 | 53 | 2 |
| 8 | 37 | 37 | 2 |
| *** 6 11 L *** | | | |
| 1 | 31 | 21 | 3 |
| 3 | 22 | 15 | 4 |
| 5 | 29 | 21 | 3 |
| *** 7 0 L *** | | | |
| 1 | 143 | 150 | 3 |
| 3 | 203 | 194 | 3 |
| 5 | 404 | 370 | 6 |
| 7 | 275 | 239 | 4 |
| 9 | 171 | 166 | 3 |
| 11 | 71 | 51 | 3 |
| 13 | 32 | 26 | 5 |
| 15W | 0 | -3 | 23 |
| *** 7 1 L *** | | | |
| 0 | 119 | 117 | 2 |
| 2 | 128 | 120 | 3 |
| 4 | 329 | 311 | 5 |
| 6 | 443 | 402 | 7 |
| 8 | 291 | 273 | 5 |
| 10 | 116 | 92 | 3 |
| 12W | 0 | 8 | 35 |
| 14W | 0 | -5 | 27 |
| 16 | 25 | 32 | 3 |
| *** 7 2 L *** | | | |
| 1 | 276 | 244 | 4 |
| 3 | 158 | 146 | 3 |
| 5 | 117 | 101 | 3 |
| 7 | 56 | -47 | 4 |
| 9 | 44 | 54 | 5 |
| 11 | 83 | 83 | 3 |
| 13 | 78 | 88 | 3 |
| 15 | 47 | 54 | 3 |
| *** 7 3 L *** | | | |
| 0 | 514 | 486 | 8 |
| 2 | 338 | 328 | 5 |
| 4 | 60 | 49 | 3 |
| 6 | 112 | -112 | 3 |
| 8 | 56 | -53 | 3 |
| 10 | 68 | 60 | 3 |
| 12 | 128 | 126 | 3 |
| 14 | 96 | 104 | 2 |
| 16 | 55 | 53 | 2 |
| *** 7 4 L *** | | | |
| 1 | 56 | 50 | 3 |
| 3 | 65 | 76 | 3 |
| 5 | 26 | 13 | 7 |
| 7 | 92 | -89 | 3 |
| 9 | 42 | 41 | 4 |
| 11W | 14 | 20 | 33 |
| 13 | 26 | 30 | 5 |
| 15 | 24 | 16 | 3 |
| *** 7 5 L *** | | | |
| 0 | 223 | 208 | 4 |
| 2 | 200 | 201 | 3 |
| 4 | 63 | 71 | 3 |
| 6 | 43 | 44 | 5 |
| 8 | 54 | 47 | 4 |
| 10 | 55 | 48 | 3 |
| 12 | 58 | 58 | 3 |
| 14 | 31 | 30 | 3 |
| *** 7 6 L *** | | | |
| 1 | 118 | 108 | 2 |
| 3 | 48 | 58 | 4 |
| 5 | 68 | 66 | 3 |
| 7W | 0 | 1 | 34 |
| 9 | 41 | 54 | 4 |
| 11 | 37 | 34 | 3 |
| 13 | 32 | 35 | 3 |
| *** 7 7 L *** | | | |
| 0 | 72 | 60 | 3 |
| 2 | 79 | 72 | 3 |
| 4 | 78 | 78 | 3 |
| 6 | 142 | 138 | 3 |
| 8 | 87 | 90 | 2 |
| 10 | 35 | 37 | 4 |
| 12 | 28 | 30 | 3 |
| *** 7 8 L *** | | | |
| 1 | 95 | 96 | 2 |
| 3 | 99 | 93 | 2 |
| 5 | 143 | 140 | 3 |
| 7 | 92 | 97 | 2 |
| 9 | 72 | 77 | 2 |
| 11 | 40 | 36 | 2 |
| *** 7 9 L *** | | | |
| 0 | 23 | -22 | 6 |
| 2 | 29 | 28 | 5 |
| 4 | 92 | 87 | 2 |
| 6 | 119 | 121 | 2 |
| 10 | 40 | 38 | 2 |
| *** 7 10 L *** | | | |
| 1 | 70 | 69 | 2 |
| 5 | 107 | 105 | 2 |
| 7 | 78 | 79 | 2 |
| *** 7 11 L *** | | | |
| 0 | 63 | 65 | 2 |
| 2 | 56 | 55 | 2 |
| *** 8 0 L *** | | | |
| 0 | 88 | 88 | 3 |
| 2 | 107 | 106 | 2 |
| 4 | 119 | -87 | 2 |
| 6 | 137 | -131 | 3 |
| 8 | 115 | -97 | 3 |
| 10W | 10 | -13 | 35 |
| 12 | 37 | 49 | 4 |
| 14 | 29 | 24 | 4 |
| *** 8 1 L *** | | | |
| 1 | 139 | 120 | 3 |
| 3 | 84 | 85 | 3 |
| 5 | 79 | 52 | 3 |
| 7 | 106 | -87 | 3 |
| 9 | 55 | 52 | 4 |
| 11 | 33 | 29 | 5 |
| 13 | 42 | 43 | 3 |
| 15 | 26 | 20 | 3 |
| *** 8 2 L *** | | | |
| 0 | 186 | 173 | 3 |
| 2 | 191 | -184 | 3 |
| 4 | 48 | 51 | 4 |
| 6 | 20 | -25 | 10 |
| 8 | 32 | 29 | 6 |
| 10 | 48 | 40 | 4 |
| 12 | 62 | 65 | 3 |
| 14 | 40 | 38 | 3 |
| *** 8 3 L *** | | | |
| 1 | 493 | 459 | 7 |
| 3 | 274 | 256 | 4 |
| 5 | 175 | 155 | 3 |
| 7 | 42 | 46 | 5 |
| 9 | 114 | 114 | 3 |
| 11 | 129 | 128 | 3 |
| 13 | 121 | 126 | 2 |
| 15 | 64 | 61 | 2 |
| *** 8 4 L *** | | | |
| 0 | 30 | 9 | 6 |
| 2 | 39 | 36 | 5 |
| 4 | 80 | 72 | 3 |
| 6 | 154 | 153 | 3 |
| 8 | 119 | 117 | 3 |
| 10 | 40 | 39 | 4 |
| 12 | 27 | 24 | 4 |
| 14W | 0 | -2 | 15 |
| *** 8 5 L *** | | | |
| 1 | 27 | -29 | 6 |
| 3 | 52 | 43 | 4 |
| 5 | 214 | 209 | 3 |
| 7 | 163 | 156 | 3 |
| 9 | 92 | 92 | 2 |
| 11 | 23 | 3 | 5 |
| 13 | 25 | -22 | 3 |
| *** 8 6 L *** | | | |
| 0W | 0 | -6 | 35 |
| 2 | 40 | 29 | 4 |
| 4 | 50 | 48 | 4 |
| 6 | 68 | 69 | 3 |
| 8 | 45 | 47 | 3 |
| 10 | 22 | 17 | 5 |
| 12W | 0 | 2 | 16 |
| *** 8 7 L *** | | | |
| 1 | 76 | 63 | 3 |
| 3 | 100 | 98 | 2 |
| 5 | 106 | 105 | 2 |
| 7 | 66 | 64 | 2 |
| 9 | 61 | 63 | 2 |
| 11 | 27 | 22 | 3 |
| *** 8 8 L *** | | | |
| 0 | 165 | 173 | 3 |
| 2 | 155 | 166 | 3 |
| 4 | 126 | 125 | 2 |
| 6 | 88 | 92 | 2 |
| 10 | 66 | 63 | 2 |
| *** 8 9 L *** | | | |
| 1 | 90 | 98 | 2 |
| 3 | 82 | 83 | 2 |
| *** 8 10 L *** | | | |
| 0 | 87 | 90 | 2 |
| 2 | 92 | 90 | 2 |
| 4 | 102 | 105 | 2 |
| *** 9 0 L *** | | | |
| 1 | 181 | 158 | 3 |
| 3 | 75 | 72 | 3 |
| 5 | 67 | 49 | 3 |
| 7 | 75 | -76 | 3 |
| 9 | 55 | 56 | 3 |
| 11 | 24 | 25 | 6 |
| *** 9 1 L *** | | | |
| 0 | 88 | 78 | 3 |
| 2 | 131 | 110 | 3 |
| 4 | 77 | 79 | 3 |
| 6 | 173 | 154 | 3 |
| 8 | 113 | 112 | 3 |
| 10 | 42 | 39 | 4 |
| 12 | 44 | 43 | 3 |
| 14W | 0 | -5 | 14 |
| *** 9 2 L *** | | | |
| 1 | 53 | -50 | 3 |
| 3 | 37 | 42 | 5 |
| 5 | 238 | 222 | 4 |
| 7 | 164 | 157 | 3 |
| 9 | 111 | 112 | 3 |
| 11W | 9 | 8 | 26 |
| 13 | 22 | -18 | 4 |
| *** 9 3 L *** | | | |
| 0 | 183 | 168 | 3 |
| 2 | 180 | 157 | 3 |
| 4 | 141 | 128 | 3 |
| 6 | 149 | 137 | 3 |
| 8 | 102 | 101 | 3 |
| 10 | 54 | 57 | 3 |
| 12 | 51 | 48 | 2 |
| *** 9 4 L *** | | | |
| 1 | 160 | 143 | 3 |
| 3 | 155 | 146 | 3 |
| 5 | 162 | 154 | 3 |
| 7 | 93 | 86 | 2 |
| 9 | 94 | 92 | 2 |
| 11 | 56 | 48 | 2 |
| 13 | 28 | 31 | 2 |
| *** 9 5 L *** | | | |
| 0 | 30 | 13 | 6 |
| 2 | 83 | 78 | 3 |
| 4 | 124 | 126 | 3 |
| 6 | 135 | 135 | 3 |
| 8 | 120 | 121 | 2 |
| 10 | 56 | 45 | 2 |
| 12W | 10 | 6 | 14 |
| *** 9 6 L *** | | | |
| 1 | 111 | 117 | 2 |
| 3 | 91 | 91 | 2 |
| 5 | 75 | 70 | 2 |
| 7 | 57 | 52 | 2 |
| 9 | 63 | 59 | 2 |
| 11 | 52 | 45 | 2 |
| *** 9 7 L *** | | | |
| 0 | 117 | 114 | 2 |
| 2 | 83 | 88 | 2 |
| 4 | 63 | 58 | 2 |
| 6 | 52 | 49 | 3 |
| 8 | 58 | 52 | 2 |
| 10 | 45 | 43 | 2 |
| *** 9 8 L *** | | | |
| 1 | 137 | 149 | 2 |
| 3 | 118 | 118 | 2 |
| 7 | 100 | 96 | 2 |
| ***10 0 L *** | | | |
| 0 | 60 | -65 | 3 |
| 2 | 35 | 23 | 5 |
| 4 | 50 | 40 | 3 |
| 6 | 110 | 99 | 3 |
| 8 | 66 | 68 | 3 |
| 10 | 23 | 7 | 5 |
| ***10 1 L *** | | | |
| 1 | 47 | 30 | 4 |
| 3 | 53 | 46 | 3 |
| 5 | 125 | 113 | 3 |
| 7 | 52 | 41 | 3 |
| 9 | 62 | 60 | 3 |
| 11W | 14 | 4 | 19 |
| ***10 2 L *** | | | |
| 0 | 48 | 33 | 4 |
| 2 | 124 | 111 | 3 |
| 4 | 151 | 150 | 3 |
| 6 | 180 | 164 | 3 |
| 8 | 141 | 137 | 3 |
| 10 | 60 | 51 | 2 |
| 12 | 15 | 16 | 5 |
| ***10 3 L *** | | | |
| 1 | 155 | 149 | 3 |
| 3 | 132 | 124 | 3 |
| 5 | 114 | 101 | 2 |
| 7 | 67 | 63 | 3 |
| 9 | 86 | 85 | 2 |
| 11 | 59 | 58 | 2 |
| ***10 4 L *** | | | |
| 0 | 300 | 297 | 5 |
| 2 | 242 | 240 | 4 |
| 4 | 140 | 132 | 3 |
| 6 | 96 | 92 | 2 |
| 8 | 93 | 95 | 2 |
| 10 | 92 | 88 | 2 |
| ***10 5 L *** | | | |
| 1 | 75 | 75 | 2 |
| 3 | 80 | 75 | 2 |
| 5 | 113 | 114 | 2 |
| 7 | 104 | 105 | 2 |
| 9 | 73 | 71 | 2 |
| ***10 6 L *** | | | |
| 0 | 118 | 118 | 2 |
| 2 | 97 | 101 | 2 |
| 4 | 116 | 118 | 2 |
| 6 | 120 | 120 | 2 |
| 8 | 93 | 89 | 2 |
| ***10 7 L *** | | | |
| 1 | 58 | 61 | 2 |
| 5 | 42 | 35 | 2 |
| 7 | 13 | 17 | 5 |
| ***10 8 L *** | | | |
| 2 | 43 | 46 | 2 |
| 4 | 38 | 40 | 2 |
| ***11 0 L *** | | | |
| 1 | 118 | 107 | 2 |
| 3 | 99 | 92 | 2 |
| 5 | 111 | 97 | 2 |
| 7 | 49 | 45 | 3 |
| ***11 1 L *** | | | |
| 0 | 109 | 100 | 2 |
| 2 | 115 | 106 | 2 |
| 4 | 55 | 45 | 3 |
| 6 | 42 | 36 | 3 |
| 8 | 49 | 46 | 3 |
| 10 | 37 | 35 | 2 |
| ***11 2 L *** | | | |
| 1 | 122 | 120 | 2 |
| 3 | 102 | 99 | 2 |
| 5 | 136 | 134 | 3 |
| 7 | 106 | 106 | 2 |
| 9 | 89 | 88 | 2 |
| ***11 3 L *** | | | |
| 0 | 96 | 94 | 2 |
| 2 | 100 | 98 | 2 |
| 4 | 109 | 106 | 2 |
| 6 | 121 | 120 | 2 |
| 8 | 105 | 96 | 2 |
| ***11 4 L *** | | | |
| 1 | 215 | 217 | 3 |
| 3 | 162 | 157 | 3 |
| 5 | 118 | 114 | 2 |
| 7 | 74 | 68 | 2 |
| 9 | 60 | 68 | 2 |
| ***11 5 L *** | | | |
| 0 | 59 | 52 | 2 |
| 2 | 53 | 54 | 2 |
| 4 | 56 | 55 | 2 |
| 6 | 28 | 26 | 3 |
| ***11 6 L *** | | | |
| 1 | 30 | 11 | 3 |
| 3 | 32 | 32 | 3 |
| 5 | 23 | 18 | 3 |
| ***11 7 L *** | | | |
| 0 | 70 | 64 | 2 |
| 2 | 36 | 39 | 2 |
| ***12 0 L *** | | | |
| 0 | 136 | 133 | 2 |
| 2 | 134 | 129 | 2 |
| 4 | 101 | 93 | 2 |
| ***12 1 L *** | | | |
| 1 | 84 | 79 | 2 |
| 3 | 73 | 63 | 2 |
| 5 | 76 | 69 | 2 |
| 7 | 36 | 33 | 2 |
| ***12 2 L *** | | | |
| 0 | 59 | 55 | 2 |
| 2 | 64 | 67 | 2 |
| 4 | 61 | 58 | 2 |
| 6 | 40 | 44 | 2 |
| ***12 3 L *** | | | |
| 1 | 20 | 13 | 6 |
| 3 | 32 | 38 | 3 |
| 5 | 41 | 42 | 2 |
| ***12 4 L *** | | | |
| 0 | 109 | 107 | 2 |
| 2 | 87 | 85 | 2 |
| 4 | 24 | 29 | 3 |
| ***12 5 L *** | | | |
| 1 | 134 | 130 | 2 |
| 3 | 80 | 82 | 2 |
| ***13 1 L *** | | | |
| 0 | 25 | 16 | 3 |
| 2 | 16 | 23 | 4 |
| ***13 2 L *** | | | |
| 1 | 54 | 51 | 2 |

highest intensity, marked $X$ in the table, were excluded in the final refinement cycles as subject to extinction error. The final atomic parameters and their standard errors appear in Table 2. The root-mean-square atomic vibrational amplitudes are given in Table 3.

As in the case of the 3,5-dimethylpyridine complex compound (part I), the agreement between the calculated and observed $F^2$ values is not so close as one would desire, and the coordinates of the perchlorate ion do not describe a regular tetrahedral ion. In fact, in the present case the configuration of the ion is much less satisfactory than in the other case. The inadequacy of the model for the disorder of the perchlorate ion

Table 3. *Root-mean-square atomic displacements in the directions of the principal axes of the thermal ellipsoids*

| | R.m.s.d. (Å) in direction of axis | | |
| | 1 | 2 | 3 |
|---|---|---|---|
| Ni | 0·176 (2) | 0·176 (2) | 0·263 (2) |
| N | 0·179 (3) | 0·191 (3) | 0·261 (3) |
| C(1) | 0·208 (3) | 0·237 (3) | 0·262 (3) |
| C(2) | 0·198 (3) | 0·239 (3) | 0·293 (3) |
| C(3) | 0·185 (4) | 0·197 (4) | 0·324 (5) |
| C(4) | 0·226 (8) | 0·366 (11) | 0·399 (11) |
| C(5) | 0·186 (5) | 0·264 (4) | 0·398 (6) |
| Cl | 0·214 (3) | 0·294 (4) | 0·353 (5) |
| O(1) | 0·285 (7) | 0·407 (6) | 0·407 (6) |
| O(2) | 0·241 (6) | 0·395 (4) | 0·395 (4) |
| O(3) | 0·285 (18) | 0·329 (23) | 0·496 (37) |
| O(4) | 0·253 (20) | 0·340 (20) | 0·671 (42) |

Table 2. *Parameters of the structure of* Ni(3,4-dimethylpyridine)$_2$(ClO$_4$)$_2$

The elements $\beta_{ij}$ form the matrix $\beta$ in the anisotropic temperature factor exp $(-h^T\beta h)$, where h is the vector of reflection indices. The least-squares standard errors, corresponding to the least-significant digits of the parameters, appear in parentheses. Parameters which are identically zero mark the atoms in special positions. The $\beta_{11}$ parameters marked with asterisks were constrained to be equal to the corresponding $\beta_{22}$ parameters. Each hydrogen atom, or site, is given the same identifying number as the parent carbon atom and, when necessary, an additional alphabetic character. Coordinates of only one of the six sites for half-weight hydrogen atoms on C(4) are given; the others may easily be computed.

| | 1st digit = tenths digit | | | 1st digit = hundredths digit | | | 1st digit = thousandths digit | | |
| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | 0 | 0 | 0 | 0571 (*) | 0571 (9) | 0559 (7) | 0 | 0 | 0 |
| N | 17267 (24) | 06254 (23) | 0 | 0594 (21) | 0672 (22) | 0551 (14) | −008 (17) | 0 | 0 |
| C(1) | 23454 (24) | 08719 (24) | 07403 (19) | 0861 (22) | 0983 (24) | 0554 (13) | −100 (19) | −023 (14) | −020 (14) |
| C(2) | 35940 (25) | 13535 (27) | 07551 (22) | 0859 (23) | 1015 (25) | 0654 (15) | −095 (20) | −172 (15) | −048 (16) |
| C(3) | 42296 (32) | 16130 (31) | 0 | 0660 (28) | 0692 (27) | 0847 (26) | −039 (23) | 0 | 0 |
| C(4) | 41951 (91) | 15647 (102) | 16174 (71) | 1581 (89) | 2300 (128) | 1090 (63) | −637 (93) | −444 (64) | −065 (74) |
| C(5) | 55763 (39) | 21560 (43) | 0 | 0760 (34) | 1175 (46) | 1281 (41) | −251 (34) | 0 | 0 |
| Cl | 0507 (15) | 0318 (24) | 2841 (2) | 177 (15) | 206 (15) | 040 (1) | −33 (8) | −18 (3) | 04 (4) |
| O(1) | 0 | 0 | 21412 (43) | 3067 (*) | 3067 (78) | 0658 (31) | 0 | 0 | 0 |
| O(2) | 0 | 0 | 36600 (33) | 2880 (*) | 2880 (67) | 0472 (25) | 0 | 0 | 0 |
| O(3) | 0893 (44) | 1470 (31) | 2698 (14) | 413 (54) | 224 (35) | 074 (10) | −99 (36) | −06 (23) | −15 (16) |
| O(4) | 1778 (25) | 0257 (85) | 2802 (13) | 181 (26) | 805 (105) | 079 (8) | 56 (61) | −24 (12) | 84 (27) |
| H(1) | 18 | 07 | 14 | | | | | | |
| H(2) | 39 | 15 | 14 | | | | | | |
| H(4a) | 441 | 249 | 17 | | | | | | |
| H(5b) | 622 | 143 | 0 | | | | | | |
| H(5c) | 570 | 270 | −052 | | | | | | |
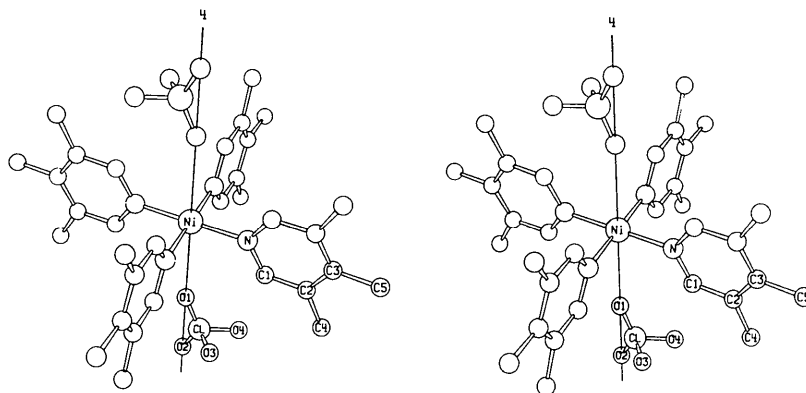


Fig. 1. Stereoscopic drawing of the disordered square-planar cation in Ni(3,4-dimethylpyridine)$_4$(ClO$_4$)$_2$. Each carbon atom C(4) is shown in both of the sites in which it is distributed because of rotational disorder about the axis from N to C(5). Each of the nearby disordered perchlorate ions is shown in only one of its four equivalent orientations about the 4-fold axis.

probably accounts largely for the fact that $\sigma_1$ is so much greater than the value unity expected at the end of refinement. In this connection we remark that the oxygen atoms O(1) and O(2) are not required by symmetry to be exactly on the fourfold axis. The axial positions do make good sense, however, in terms of the packing of the perchlorate ions in the crystal (see *Discussion*).

It seems to us that the question of whether or not the space group is actually $I4/m$, as we have assumed in all stages beyond the calculation of the Patterson map, has been made irrelevant by the structure we have found. Any departure of the symmetry from $I4/m$ toward either $I4$ or $I\bar{4}$ must be very slight and of little chemical relevance. Even if we had a suggestion as to the nature of such a departure, it would be very difficult to check because of the perturbing effects of the disorder of arrangement of the perchlorate ions. It is worth noting specifically that the Patterson map shows that there would be the same problems of disorder with respect to the organic ligands and the perchlorate ions for either space group $I4$ or $I\bar{4}$.

## Discussion

In spite of the vexing problem of disorder of the perchlorate ions, the parameters of the remainder of the structure appear to be determined with fairly good precision; and the principal questions of interest with reference to the structure of Ni(3,4-dimethylpyridine)$_4$-(ClO$_4$)$_2$ have been answered. The perchlorate ions are not coordinated to nickel in this substance; the nearest-neighbor nickel–oxygen distance, Ni–O(1), is 3·343(7) Å, much too great a distance for a chemical linkage. The Ni(3,4-dimethylpyridine)$_4^{2+}$ ion exhibits square-planar coordination of the ligands. The symmetry of the disordered ion is, in the statistical sense, that of point group $4/m$; the planes of the pyridine groups are perpendicular to the mirror $m$. The bonds Ni–N are ro-

tated 19·9° from coincidence with the directions of the lattice vectors **a** and **b**. A stereoscopic view of the complex ion is shown in Fig. 1.

Bond lengths and angles in the ion are shown in Table 4.* Because of the rotational disorder about the axis N–C(3) (and possibly because of a slight departure from the assumed symmetry $I4/m$), the bond lengths and angles given for the organic ligand are not those of a real unit 3,4-dimethylpyridine, which would not be required to have exact mirror symmetry even for the ring atoms alone. Nevertheless, the structure of the ligand is quite acceptable (see part I for comparison with the structure of the 3,5-dimethylpyridine ligand and with the structure of pyridine). Even the distances and angles involving H(1) and H(2), attached to C(1) and C(2), seem quite sensible if allowance is made for the considerable uncertainties in the coordinates of the hydrogen atoms. The various torsion angles given in Table 4 for the bonds of the pyridine ring show that there are slight deviations from exact coplanarity of the atoms of the organic ligand; however, we do not consider these deviations to be significant.

Even though the description of the perchlorate ion is in general unsatisfactory (see Table 4), it is gratifying that the distance 2·371(9) Å between the two atoms O(1) and O(2), which are the only atoms of the perchlorate groups whose coordinates are reasonably well determined, is quite close to the distance 2·34 Å expected for a regular tetrahedral perchlorate ion with Cl–O bond lengths 1·43(2) Å (*Tables of Interatomic Distances*, 1965, page S8s).

The Ni–N bond length of 1·897(3) Å is comparable to other Ni–N distances in planar complexes of nickel: 1·850(15) Å in bisdimethylgloximatonickel(II) (Wil-

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\* The atom designations in Table 4 conform to the labelling of the asymmetric unit in Fig. 1. When necessary, alphabetic characters are added to the designations to distinguish atoms of the asymmetric unit ($A$) from equivalent atoms ($B$) generated by the mirror at $z = 0$.

Table 4. *Bond lengths and angles in the structure of* Ni(3,4-*dimethylpyridine*)$_4$(ClO$_4$)$_2$

Each angle specified by four atoms, as $a$–$b$–$c$–$d$, is a torsion angle, defined to be the angle measured clockwise from the projection of $ba$ to the projection of $cd$ viewed in the direction of $bc$. The indicated standard errors were calculated from the least-squares covariance matrix. For the key to the numbering of atoms see Fig. 1 and the text.

| | | | |
|---|---|---|---|
| Ni—N | 1·897 (3) Å | N——C(1)--C(2)—C(3) | 1·0 (4)° |
| N——C(1) | 1·345 (3) | N——C(1)—C(2)—C(4) | −178·8 (5) |
| C(1)—C(2) | 1·382 (4) | | |
| C(2)—C(3) | 1·376 (4) | C(1$A$)-C(2$A$)-C(3$A$)-C(2$B$) | −1·3 (5) |
| C(2)—C(4) | 1·499 (10) | C(1)—C(2)—C(3)—C(5) | 179·0 (3) |
| C(3)—C(5) | 1·500 (5) | C(4)—C(2)—C(3)—C(5) | −1·2 (7) |
| | | C(4$A$)-C(2$A$)-C(3$A$)-C(2$B$) | 178·5 (5) |
| Ni——N——C(1) | 120·7 (2)° | | |
| C(1$A$)-N——C(1$B$) | 118·5 (3) | Cl——O(1) | 1·256 (6) Å |
| N——C(1)-C(2) | 121·7 (3) | Cl——O(2) | 1·420 (5) |
| C(1)—C(2)-C(3) | 120·1 (3) | Cl——O(3) | 1·27 (4) |
| C(1)—C(2)-C(4) | 117·0 (5) | Cl——O(4) | 1·32 (3) |
| C(3)—C(2)-C(4) | 123·0 (4) | | |
| C(2$A$)-C(3)-C(2$B$) | 118·0 (3) | O(1)—Cl——O(2) | 125 (1)° |
| C(2)—C(3)-C(5) | 121·0 (2) | O(1)—Cl——O(3) | 103 (2) |
| Ni——N——C(3) | 178·4 (2) | O(1)—Cl——O(4) | 111 (2) |
| C(1$B$)-N——C(1$A$)-C(2) | −0·7 (5) | O(2)—Cl——O(3) | 119 (2) |
| Ni——N——C(1)—C(2) | −178·6 (2) | O(2)—Cl——O(4) | 114 (2) |
| | | O(3)--Cl——O(4) | 74 (2) |

liams, Wohlauer & Rundle, 1959; see also Godycki & Rundle, 1953); 1·868(4) and 1·880(4) Å in bisglyoximatonickel(II) (Calleri, Ferraris & Viterbo, 1967); 1·855(5) Å in bis-salicylaldoximatonickel(II) (Srivastava, Lingafelter & Jain, 1967; see also Merritt, Guare & Lessor, 1956); 1·92(1) Å in bis-(N-methylsalicylaldiminato)nickel(II) (Fox & Lingafelter, 1967); 1·911(14) Å in bisthiosemicarbazidatonickel(II) (Cavalca, Nardelli & Fava, 1962).

The relation of the perchlorate ions to the Ni(3,4-dimethylpyridine)$_4^{2+}$ complex ion is shown in Fig.1, and the arrangement of both kinds of ion in the unit cell is shown in Fig.2. In the latter figure only the location of the centroid of each disordered perchlorate ion is shown. Atom O(1) of each perchlorate group is in contact with four atoms H(1) of a given complex ion arranged symmetrically about a fourfold axis, the O(1)···H(1) distance being 2·31 Å* and the related O(1)···C(1) distance 3·386 Å. Atom O(2) of each perchlorate group is in contact with four C(5) methyl groups of four different complex ions arranged about the same fourfold axis; the distance O(2)···C(5) is 3·65 Å. Each atom O(2) is also at the distance 3·67 Å from each of four equivalent sites for the disordered C(4) methyl groups. The orientational stability of the O(1)···O(2) axis of the perchlorate ion is consistent with the nesting of O(1) among the atoms H(1) and of O(2) among the methyl groups.

The only short distances between sites of atoms not bonded to each other are distances between possible sites for the disordered atoms O(3), O(4), Cl, and C(4):

C(4A)···O(3C), 2·30(3) Å; C(4A)···Cl(C), 3·35(2) Å; C(4A)···O(4D), 2·23(4) Å; C(4A)···Cl(D), 3·35(2) Å; C(4A)···C(4E), 3·63(2) Å; C(4A)···C(4D), 3·72(2) Å.

Here C(4A) denotes the site specified by the coordinates given for C(4) in Table 2; the other sites are specified by the appropriate coordinates in Table 2 transformed as follows: (C) $\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}-z$; (D) $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$; (E) $1-x,\bar{y},z$. The two distances C(4)···C(4) are in

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* This distance is surely slightly shorter than the actual distance, consistent with the fact that the apparent C(1)–H(1) distance of 1·18 Å is somewhat long.

fact at the lower end of the distance range for contacts between methyl groups; for example, a methyl··· methyl distance of 3·702(5) Å has been found in the structure of copper acetate monohydrate (Chidambaram & Brown, 1965). The other inter-site distances quoted above clearly cannot represent real distances between atoms. However, since only one-fourth of the sites for O(3), O(4), and Cl and one-half of those of C(4) are occupied, these disordered atoms can be distributed in such a way as to avoid the impossible 'contacts'.

The differences between the structure of Ni(3,4-dimethylpyridine)$_4$(ClO$_4$)$_2$ and that of Ni(3,5-dimethylpyridine)$_4$(ClO$_4$)$_2$ are quite striking, especially when one considers that the only difference between the organic ligands in the two compounds is in the location of a methyl group. The position of this group determines whether the perchlorate ions are coordinated or not, what the orientation of the organic ligands is with respect to the plane of the nickel and nitrogen atoms, and whether the Ni–N bond length takes the value 1·897 Å or 2·093 Å. Considering only the geometry of the octahedral complex Ni(3,5-dimethylpyridine)$_4$-(ClO$_4$)$_2$ and the square complex ion Ni(3,4-dimethylpyridine)$_4^{2+}$, we see no reason why either substituted pyridine ligand should not equally well have produced a compound with nickel perchlorate of the type found for the other ligand. There is no steric feature within the ion Ni(3,4-dimethylpyridine)$_4^{2+}$ which would prevent it from assuming a propeller-like arrangement of the organic ligands and accepting two perchlorate ions in coordination; nor is there any steric feature which would preclude the formation of a square-planar ion Ni(3,5-dimethylpyridine)$_4^{2+}$.

It seems probable that secondary valence forces and the energy of packing in the crystalline state are important factors in determining the type of structure, paramagnetic octahedral or diamagnetic square-planar, that each of these compounds exhibits. If other factors, particularly the energy of covalent bonding and electrostatic energy, are nearly in balance for the two structure types, the crystal energy can be the decisive factor. The packing of one structure type is disrupted, so to
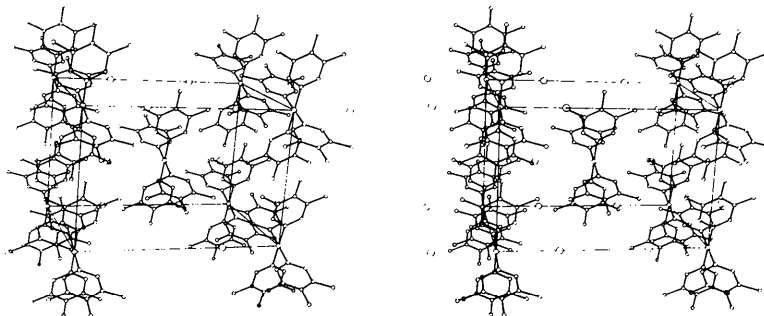


Fig. 2. Stereoscopic drawing showing the arrangement of ions in the crystal structure of Ni(3,4-dimethylpyridine)$_4$(ClO$_4$)$_2$. The lattice vector c is approximately horizontal, and the parallelepiped shown outlines one unit cell. Each disordered atom C(4) is shown in both of two equivalent sites. The centroid of each disordered perchlorate ion is indicated by a circle.

speak, by the shift of a methyl group; the process of readjustment to a new stable crystal structure includes a change in the coordination to the other structure type.

It is known (Buffagni, Vallarino & Quagliano, 1964) that the blue compound $Ni(3,5\text{-dimethylpyridine})_4\text{-}(ClO_4)_2$ dissociates in dichloromethane solution to give free perchlorate ions and the diamagnetic and presumably square-planar cation $Ni(3,5\text{-dimethylpyridine})_4^{2+}$. The solution is yellow and nearly identical in its electronic spectrum with a solution of the 3,4-dimethylpyridine complex compound. On the other hand, the blue paramagnetic complex $Ni(pyridine)_4(ClO_4)_2$ appears not to dissociate in dichloromethane (Rosenthal & Drago, 1965), though it does so in nitromethane. These observations are consistent with the notion that secondary valence forces play an important part in determining the type of coordination of nickel(II) for this series of compounds in the solid state.

For the list of computer programs used in this work see part I.

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# Die Kristallstruktur des Botryogens

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Botryogen from the Rammelsberg mine near Goslar (Germany), $Fe^{3+}(Zn,Mn,Mg,Fe^{2+})(SO_4)_2OH \cdot 7H_2O$, crystallizes in the monoclinic space group $P2_1/n$, $a_0 = 10.526$, $b_0 = 17.872$, $c_0 = 7.136$ Å, $\beta = 100.13°$, $Z = 4$. The crystal structure has been determined by three-dimensional Fourier methods, and has been refined by the full-matrix least-squares technique with isotropic temperature factors (using 933 observed photographic data) to $R = 0.059$. All metal ions are surrounded octahedrally by oxygen atoms of OH or $H_2O$. The bond distances are normal. The $Fe^{3+}$ octahedra form infinite chains parallel to the $c$ axis. Only hydrogen bonds are active between chains. One of the seven water molecules is not linked with any cation.

Der Zn-reiche Botryogen aus dem 'Alten Mann' im Rammelsberg bei Goslar/Harz wurde von Zemann (1961) neu bearbeitet. Nach diesen Untersuchungen hat das Mineral die chemische Zusammensetzung $M_IM_{II}(SO_4)_2OH \cdot 7H_2O$, mit $M_I = Fe^{3+}$ und $M_{II} =$ $(Zn_{0,47}, Mn_{0,25}, Mg_{0,20}, Fe^{2+}_{0,08})$, und ist monoklin: Raumgruppe $P2_1/n (C_{2h}^5)$. Die rotbraunen Kristalle sind prismatisch nach [001] ausgebildet und erreichen eine Grösse bis zu einigen Millimetern. Die wichtigsten Formen sind $\{110\}$, $\{\bar{1}01\}$, $\{120\}$ und $\{010\}$. Den Habitus bestimmen $\{110\}$ und $\{\bar{1}01\}$. Die in der genannten Arbeit angegebenen Gitterkonstanten sind: $a_0 = 10,51 \pm 0,02$, $b_0 = 17,85 \pm 0,03$, $c_0 = 7,14 \pm 0,02$ Å; $\beta =$

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