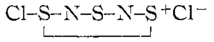
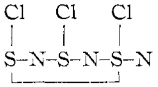
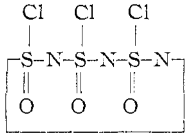
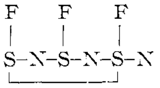
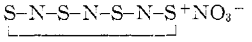
Table III

Selected Bond Lengths (A) in Some Azyl Ring Systems

| Formula | S–S | S–N | S–Cl | Ref |
|---|---|---|---|---|
|  $Cl-S-N-S-N-S^+Cl^-$ | 2.136 | 1.543–1.617 | 2.168 | This work |
|  $\overset{Cl}{S}-N-\overset{Cl}{S}-N-\overset{Cl}{S}-N$ | | 1.600–1.614 | 2.084–2.150 | 10 |
|  $\underset{O}{\overset{Cl}{S}}-N-\underset{O}{\overset{Cl}{S}}-N-\underset{O}{\overset{Cl}{S}}-N$ | | 1.546–1.578 | 1.991–1.999 | 9 |
|  $\overset{F}{S}-N-\overset{F}{S}-N-\overset{F}{S}-N$ | | 1.540–1.660 | | 11 |
|  $S-N-S-N-S-N-S^+NO_3^-$ | 2.064 | 1.493–1.582 | | 12 |
| $N_4S_4H_4$ | | 1.65 | | 13 |

is 0.188 A below the plane, and the opposing N(2) atom is 0.140 A above the plane.

The five-membered ring in $S_3N_2Cl_2$ is the smallest such ring system in a series of cyclic azyl systems. Six-membered rings are present in $(NSOCl)_3$,[9] $(NSCl)_3$,[10] and $(NSF)_3$;[11] a seven-membered ring is present in $S_4N_3NO_3$;[12] and an eight-membered ring in $N_4S_4H_4$.[13] In all these cases the nitrogens are separated by sulfur, and halogen, when present, is bonded to sulfur. Table III shows a comparison of the common bonds in these compounds.

Figure 2 shows the packing in the crystal as seen in projection down the *c* axis.

**Acknowledgment.**—We thank Professor William Jolly, who first brought these substances to our attention, Dr. Norman Logan and Dr. Keith Maguire, who both stimulated our interest and prepared the material for the investigation, and Dr. Kenneth Wynne, who measured the density for our preliminary study of the crystal.

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(9) A. C. Hazell, G. A. Wiegers, and A. Vos, *Acta Cryst.*, **20**, 192 (1966).

(10) G. A. Wiegers and A. Vos, *ibid.*, **20**, 192 (1966).

(11) G. A. Wiegers and A. Vos, *ibid.*, **14**, 562 (1961).

(12) A. W. Cordes, R. F. Kruh, and E. K. Gordon, *Inorg. Chem.*, **4**, 681 (1965).

(13) E. W. Lund and S. R. Svendsen, *Acta Chem. Scand.*, **11**, 940 (1957).

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# The Crystal Structure of Bis(ethylenediamine)palladium(II) Chloride

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The crystal structure of bis(ethylenediamine)palladium(II) chloride has been determined by three-dimensional X-ray diffraction techniques. The space group is $P\bar{1}$ with $a = 6.8607 \pm 0.0004$ A, $b = 8.3610 \pm 0.0008$ A, $c = 4.9940 \pm 0.0003$ A, $\alpha = 97.716 \pm 0.006°$, $\beta = 100.683 \pm 0.005°$, $\gamma = 108.571 \pm 0.006°$, and $Z = 1$. These cell parameters were determined by a least-squares refinement of thirty $2\theta$ values measured on a single-crystal diffractometer. The errors indicated are the estimated standard deviations as obtained from this refinement and, as such, measure the precision of the determination and not necessarily the accuracy. The structure consists of discrete $[Pd(en)_2]^{2+}$ and $Cl^-$ ions held together in layers parallel to (010) by a network of $N-H \cdots Cl$ hydrogen bonds. The N–Cl distances vary from 3.217 to 3.357 A. The palladium ion is four-coordinated by the nitrogen atoms of the ethylenediamine ligands in a planar configuration with an average Pd–N distance of 2.036 A.

## Introduction

As part of a series of investigations carried out in this laboratory into the configuration of the ethylenediamine (en) ligand in coordination compounds we have determined the crystal structure of bis(ethylenediamine)palladium(II) chloride, $Pd[NH_2(CH_2)_2NH_2]_2Cl_2$. Cox and Preston[1] report that $Pd(en)_2Cl_2$ is isomorphous with $Pt(en)_2Cl_2$ and has almost identical cell dimensions. They report $Pt(en)_2Cl_2$ as crystallizing in space group $P\bar{1}$ and having lattice parameters as follows: $a = 8.37$ A, $b = 4.95$ A, $c = 6.86$ A, $\alpha = 100° 46'$, $\beta = 111° 40'$, $\gamma = 81° 56'$. When this cell is placed in the standardized form as recommended

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(1) E. G. Cox and G. H. Preston, *J. Chem. Soc.*, 1089 (1933).

by Donnay[2] one obtains: $a = 6.86$ A, $b = 8.37$ A, $c = 4.95$ A, $\alpha = 98° 4'$, $\beta = 100° 46'$, $\gamma = 68° 20'$. Watt and Klett[3] have also reported the space group and cell dimensions for $Pt(en)_2Cl_2$ which in the form recommended by Donnay[2] are: $a = 6.881$ A, $b = 8.339$ A, $c = 4.937$ A, $\alpha = 98° 0'$, $\beta = 100° 4'$, $\gamma = 108° 22'$, $Z = 1$, space group P1 or P$\bar{1}$ (morphology of crystal suggests P$\bar{1}$).

These two sets of cell dimensions agree in all respects except for the angle $\gamma$. We have been unable to find a cause for this disagreement. However, as explained below, it appears that those given by Watt and Klett[3] are correct.

## Experimental Section

Bis(ethylenediamine)palladium(II) chloride was prepared by the method of Kurnakow and Gwosdarew[4] by the reaction of $K_2PdCl_4$ with excess ethylenediamine. Evaporation of an aqueous solution at room temperature yielded colorless prismatic crystals which were used for the structure determination.

Oscillation and equiinclination Weissenberg photographs taken with $c$ as the rotation axis show the crystal to be triclinic. Thus the space group is either P1 or P$\bar{1}$. The latter was assumed to be the correct space group and was verified by the structure determination.

The lattice parameters were determined, using Cu K$\alpha$ (1.54178 A) radiation, from the best least-squares fit to single-crystal measurements of 30 $2\theta$ values taken on a Picker diffractometer fitted with a General Electric goniostat. They are: $a = 6.8607 \pm 0.0004$ A, $b = 8.3610 \pm 0.0008$ A, $c = 4.9940 \pm 0.0003$ A, $\alpha = 97.716 \pm 0.006°$, $\beta = 100.683 \pm 0.005°$, $\gamma = 108.571 \pm 0.006°$. The errors indicated are the estimated standard deviations as obtained from the least-squares refinement and, as such, measure the precision of the determination and not necessarily the accuracy. These values are in good agreement with those given by Watt and Klett[3] for $Pt(en)_2Cl_2$. Thus it appears that $Pd(en)_2Cl_2$ and $Pt(en)_2Cl_2$ are isomorphous as reported by Cox and Preston,[1] but that the correct cell parameters for $Pt(en)_2Cl_2$ are as given by Watt and Klett.[3] It was assumed for purposes of this structure determination that there was one molecule per cell as reported by Cox and Preston.[1] This assumption was subsequently confirmed by the successful structure determination.

The X-ray intensity data were recorded on multiple films on a Nonius integrating Weissenberg camera with Cu K$\alpha$ radiation. The photographs were integrated in one direction only (perpendicular to the rotation axis); the unidirectionally-integrated diffraction spots were then scanned normal to the direction of the camera integration using a Moll-type densitometer feeding into a Leeds and Northrup amplifier and recorder with a logarithmic slide wire. The tracings thus obtained were planimetered and the area under each peak taken as the relative intensity. Only those spots appearing within the linear response range of the film were measured. A range of intensities of 1 to 1200 was obtained.

Of the 1190 unique reflections theoretically obtainable in the Cu sphere, 1022 were recorded, 52 of which were classified as unobserved reflections and assigned an intensity equal to the minimum observable intensity.

Data were collected for levels $hk0$ through $hk4$. Intensities from different levels were placed on a common scale by use of an $h0l$ Weissenberg photograph taken in the same manner as described above. Some additional reflections on this photograph which were not obtained in the $hk0$ through $hk4$ data were included in the final data set. Lorentz and polarization factors were applied, but no correction was made for absorption or dispersion. The linear absorption coefficient for Cu radiation is 191 cm$^{-1}$ and the crystal size was 0.098 × 0.073 × 0.24 mm. It has been shown by Srivastava and Lingafelter[5] that, for this compound, the failure to make absorption corrections causes no "statistically significant" change in the atomic positions of the final structure, although the temperature factors are affected markedly.

## Determination and Refinement of the Structure

Throughout this structure determination, structure factors were calculated using scattering factors for the neutral atoms given in the International Tables for X-Ray Crystallography[6] for Pd, Cl, N, and C. Those for H were obtained from McWeeny.[7]

Isotropic temperature factors were used in the form $\exp -(B \sin^2 \theta)/\lambda^2$ and anisotropic temperature factors were in the form $\exp -{}^1/_4[B_{11}(a^*)^2h^2 + B_{22}(b^*)^2k^2 + B_{33}(c^*)^2l^2 + 2B_{12}a^*b^*hk + 2B_{12}a^*c^*hl + 2B_{23}b^*c^*kl]$. The discrepancy factor $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, where the summation is over the unique observed reflections only.

Assuming the space group P$\bar{1}$ with one molecule in the cell the Pd atom may be placed at the origin. Therefore, an initial structure factor calculation with Pd at 0, 0, 0 was made, resulting in an $R$ of 0.314. A three-dimensional electron density calculation was carried out using phases determined from this structure factor calculation. All atoms except the hydrogen atoms were found from the electron density map, and a structure factor calculation with coordinates determined from this electron density map gave an $R$ of 0.165. After three cycles of positional refinement by successive electron density calculations in which an over-all isotropic temperature factor of $B = 1.95$ A$^2$ was used for the structure factor calculations, $R$ was reduced to 0.119. Three cycles of full-matrix least-squares refinement were then carried out in which all positional and individual isotropic temperature factors were varied, except of course the position of the Pd atom which is fixed by symmetry. The resulting $R$ was 0.088. All least-squares refinements were carried out using the program ORFLS[8] as modified by Stewart for inclusion in the Crystal Structures Calculations system.[9] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was similar to that used by Hughes[10] in which $\sqrt{w} = 0$ for unobserved reflections for which $|F_c| \leq F_{min}$; $\sqrt{w} = 1$ for unobserved reflections with $|F_c| > F_{min}$ and for observed reflections with $F_o \leq 32$; $\sqrt{w} = 32/F_o$ for observed reflections with $F_o > 32$. Hydrogen atoms were then introduced in their calculated positions (C–H distance assumed to be 1.05 A, N–H distance assumed to be 0.95 A), reducing $R$ to 0.085. Each hydrogen atom

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(2) J. D. H. Donnay, "Crystal Data, Determinative Tables," 2nd ed, American Crystallographic Association, Monograph No. 5, 1963, p 24.

(3) G. W. Watt and D. S. Klett, *Acta Cryst.*, **16**, 932 (1963).

(4) N. S. Kurnakow and N. J. Gwosdarew, *Z. Anorg. Allgem. Chem.*, **22**, 384 (1899).

(5) R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 321 (1966).

(6) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

(7) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

(8) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) J. M. Stewart, "Crystal Structures Calculations System, X-Ray 63, for the IBM 709/7090/7094," Technical Report TR-64-6, University of Maryland, College Park, Md., 1964.

(10) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

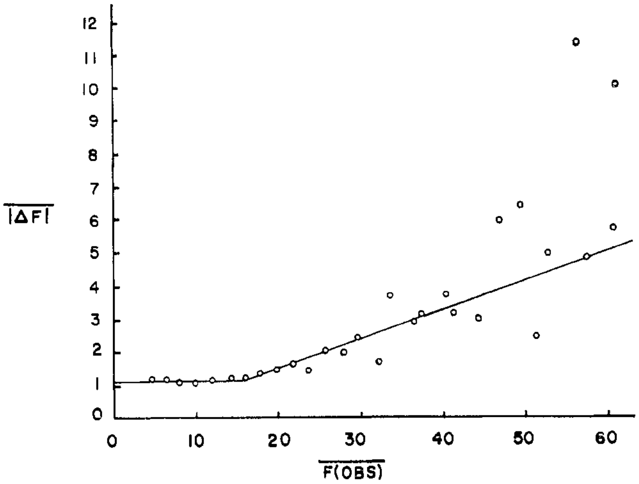

Figure 1.—Variation of $\overline{|\Delta F|}$ with $\overline{F_{OBS}}$ used to determine least-squares weighting.

was given an isotropic temperature factor equal to that of the atom to which it was attached.

At this point it was decided to use a weighting scheme for the final least-squares refinement which would be determined from an examination of the differences between observed and calculated structure factors as a function of the observed structure factor. The observed reflections were grouped in intervals of 2 units in $F_o$; the average $F_o$ of each group was plotted against the average $\overline{||F_o| - |F_c||} \equiv \overline{|\Delta F|}$ of that group. This graph is shown in Figure 1. The scatter of the points at high values of $F_o$ is caused by the small number of reflections in those groups (less than ten per group in most cases). The sloping portion of the curve can be described by the equation $\overline{|\Delta F|} = 0.0905F_o - 0.42$. Weights were assigned on the following basis: for unobserved reflections for which $|F_c| \leq F_{min}$, $\sqrt{w} = 0$; for unobserved reflections for which $|F_c| > F_{min}$, $\sqrt{w} = 1$; for observed reflections with $F_o \leq 18$, $\sqrt{w} = 1$; for observed reflections with $F_o > 18$, $\sqrt{w} = 1/\overline{|\Delta F|}$, $\overline{|\Delta F|}$ being determined from the above equation. Four cycles of full-matrix least-squares refinement varying atomic positions and anisotropic temperature factors of the nonhydrogen atoms and including the hydrogen atoms in their calculated positions, but not refining them, reduced $R$ to 0.062. After this, two cycles of least squares were run varying only the individual level scale factors, which up to this point had been held constant at their experimentally determined values. This reduced $R$ to 0.060. Then two final cycles of least squares varying atom positions and anisotropic temperature factors of the nonhydrogen atoms gave an $R$ of 0.059. For the last least-squares cycle the maximum ratio of shift to error was 0.33 and the average ratio of shift to error was 0.05. The final value of the "error of fit," $\{[\Sigma w(F_o - F_c)^2]/[\text{number of observations} - \text{number of variables}]\}^{1/2}$, was 1.06. Final atomic coordinates, the temperature factor parameters, and their estimated standard deviations for the nonhydrogen atoms are given in Table I.

Table I

Final Parameters for Nonhydrogen Atoms as Obtained from the Least-Squares Refinement[a]

| Atom | $x/a$ | $y/b$ | $z/c$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pd | 0 | 0 | 0 | 184 (2) | 182 (2) | 189 (3) | 84 (2) | 48 (2) | 18 (2) |
| Cl | −3201 (3) | 2594 (3) | 4212 (4) | 320 (8) | 416 (9) | 209 (7) | 192 (7) | 82 (7) | 29 (7) |
| N(1) | 269 (11) | −2336 (8) | 157 (15) | 328 (28) | 221 (23) | 237 (30) | 124 (21) | 146 (23) | 89 (20) |
| N(2) | −2763 (11) | −1060 (9) | 1146 (16) | 247 (26) | 260 (26) | 288 (34) | 74 (21) | 112 (22) | 31 (22) |
| C(1) | −1770 (15) | −3570 (10) | 288 (22) | 375 (38) | 204 (29) | 430 (49) | 70 (27) | 163 (33) | 105 (28) |
| C(2) | −2697 (15) | −2619 (11) | 2213 (21) | 341 (36) | 277 (32) | 368 (46) | 87 (27) | 179 (31) | 129 (29) |

[a] Positions are multiplied by $10^4$. Temperature parameters are multiplied by $10^2$. Estimated standard deviations are given in parentheses.

## Determination of Hydrogen Positions

After the final stage of least-squares refinement a difference synthesis was calculated, using only those observed reflections with sin $\theta/\lambda$ less than 0.48, for the purpose of locating the hydrogen positions. The $R$ value for the structure factors calculated excluding the hydrogen atoms was 0.067. In this difference synthesis there were thirteen peaks above 0.4 $e^-/A^3$. Eight of these (ranging in height from 0.61 to 1.09 $e^-/A^3$) were located very close to the calculated hydrogen positions and the remaining five (ranging in height from 0.55 to 0.89 $e^-/A^3$) were too distant from any atom to be considered bonded to it and were, therefore, removed from further consideration. The smallest distance of any of these latter peaks to an atom was 1.53 A to N(1). Table II contains the hydrogen positions as obtained from this difference map along with their isotropic temperature parameters. The parameters for nonhydrogen atoms as given in Table I and the parameters for hydrogen atoms as given in Table II were used to calculate the final set of structure factors given in Table III. The $R$ index of 0.059 for this

Table II

Final Parameters of the Hydrogen Atoms[a]

| Atom | $x/a$[b] | $y/b$[b] | $z/c$[b] | $B$[c] |
|---|---|---|---|---|
| H(1) | 883 | −2595 | −1058 | 272 |
| H(2) | 1417 | −2000 | 1654 | 272 |
| H(3) | −2806 | −4022 | −1667 | 342 |
| H(4) | −1717 | −4786 | 577 | 342 |
| H(5) | −4150 | −3476 | 2577 | 325 |
| H(6) | −1533 | −2131 | 4115 | 325 |
| H(7) | −4000 | −1500 | −539 | 272 |
| H(8) | −2733 | −119 | 2692 | 272 |

[a] Positions are multiplied by $10^4$. Temperature parameters are multiplied by $10^2$. [b] Determined from a final difference Fourier. [c] Set equal to temperature factor of heavy atom at end of isotropic refinement.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

| | | |
|---|---|---|
| 0,K,0 | | |
| 1 | 348 | 456 |
| 2 | 117 | -75 |
| 3 | 334 | 389 |
| 4 | 414 | 462 |
| 5 | 200 | 201 |
| 6 | 99 | 76 |
| 7 | 185 | 170 |
| 8 | 247 | 238 |
| 9 | 127 | 124 |
| 1,K,0 | | |
| 0 | 380 | 446 |
| 1 | 377 | 406 |
| 2 | 302 | 327 |
| 3 | 70 | 82 |
| 4 | 224 | 237 |
| 5 | 346 | 370 |
| 6 | 189 | 199 |
| 7 | 140 | 110 |
| 8 | 171 | 158 |
| 9 | 144 | 125 |
| 2,K,0 | | |
| 0 | 79 | 72 |
| 1 | 200 | 207 |
| 2 | 437 | 469 |
| 3 | 281 | 308 |
| 4 | 205 | 198 |
| 5 | 236 | 229 |
| 6 | 221 | 204 |
| 7 | 152 | 133 |
| 8 | 77 | 73 |
| 3,K,0 | | |
| 0 | 492 | 539 |
| 1 | 389 | 408 |
| 2 | 150 | 138 |
| 3 | 201 | 223 |
| 4 | 299 | 318 |
| 5 | 156 | 146 |
| 6 | 74 | 55 |
| 7 | 123 | 112 |
| 4,K,0 | | |
| 0 | 302 | 316 |
| 1 | 409 | 402 |
| 2 | 164 | 147 |
| 3 | 97 | 81 |
| 4 | 176 | 173 |
| 5 | 156 | 155 |
| 6 | 103 | 102 |
| 5,K,0 | | |
| 0 | 140 | 125 |
| 1 | 139 | 118 |
| 2 | 202 | 197 |
| 3 | 173 | 173 |
| 4 | 87 | 80 |
| 5 | 115 | 108 |
| 6,K,0 | | |
| 0 | 208 | 225 |
| 1 | 142 | 131 |
| 2 | 102 | 108 |
| 3 | 143 | 142 |
| 4 | 135 | 120 |
| 7,K,0 | | |
| 0 | 160 | 161 |
| 1 | 176 | 182 |
| 2 | 120 | 103 |
| 8,K,0 | | |
| 0 | 77 | 68 |
| -1,K,0 | | |
| 1 | 364 | 377 |
| 2 | 403 | 418 |
| 3 | 504 | 608 |
| 4 | 302 | 336 |
| 5 | 190 | 193 |
| 6 | 284 | 258 |
| 7 | 179 | 165 |
| 8 | 121 | 113 |
| 9 | 154 | 141 |
| 10 | 126 | 105 |
| -2,K,0 | | |
| 1 | 533 | 508 |
| 2 | 389 | 360 |
| 3 | 172 | 158 |
| 4 | 304 | 333 |
| 5 | 453 | 422 |
| 6 | 265 | 294 |
| 7 | 148 | 127 |
| 8 | 150 | 130 |
| 9 | 198 | 195 |
| 10 | 112 | 101 |
| -3,K,0 | | |
| 1 | 304 | 296 |
| 2 | 51* | 29 |
| 3 | 313 | 265 |
| 4 | 456 | 483 |
| 5 | 184 | 195 |
| 6 | 78 | 74 |
| 7 | 273 | 276 |
| 8 | 227 | 262 |
| 9 | 147 | 126 |
| 10 | 79 | 86 |
| -4,K,0 | | |
| 1 | 142 | 141 |
| 2 | 338 | 329 |
| 3 | 440 | 417 |
| 4 | 277 | 248 |
| 5 | 145 | 120 |
| 6 | 161 | 158 |
| 7 | 272 | 245 |
| 8 | 171 | 170 |
| 9 | 88 | 96 |
| 10 | 146 | 137 |
| -5,K,0 | | |
| 1 | 283 | 259 |
| 2 | 329 | 323 |
| 3 | 190 | 177 |
| 4 | 189 | 177 |
| 5 | 333 | 328 |
| 6 | 215 | 220 |
| 7 | 78* | 66 |
| 8 | 141 | 141 |
| 9 | 166 | 169 |
| 10 | 92 | 99 |
| -6,K,0 | | |
| 1 | 159 | 154 |
| 2 | 109* | 68 |
| 3 | 176 | 179 |
| 4 | 273 | 267 |
| 5 | 192 | 189 |
| 6 | 108 | 114 |
| 7 | 157 | 156 |
| 8 | 189 | 206 |
| 9 | 120 | 118 |
| -7,K,0 | | |
| 1 | 99* | 73 |
| 2 | 121 | 117 |
| 3 | 220 | 231 |
| 4 | 141 | 141 |
| 5 | 100* | 38 |
| 6 | 154 | 144 |
| 7 | 191 | 203 |
| 8 | 116 | 118 |
| -8,K,0 | | |
| 1 | 123 | 139 |
| 2 | 153 | 154 |
| 3 | 94 | 100 |
| 4 | 92 | 100 |
| 5 | 122 | 137 |
| 6 | 134 | 124 |
| 7 | 75 | 74 |
| 0,K,1 | | |
| -10 | 96 | 97 |
| -9 | 160 | 163 |
| -8 | 167 | 167 |
| -7 | 123 | 119 |
| -6 | 264 | 258 |
| -5 | 296 | 307 |
| -4 | 117 | 126 |
| -3 | 246 | 230 |
| -2 | 423 | 426 |
| 0 | 402 | 516 |
| 1 | 366 | 451 |
| 2 | 447 | 513 |
| 3 | 342 | 353 |
| 4 | 146 | 151 |
| 5 | 224 | 222 |
| 6 | 237 | 234 |
| 7 | 121 | 107 |
| 8 | 124 | 115 |
| 9 | 162 | 140 |
| 1,K,1 | | |
| -10 | 68* | 52 |
| -9 | 151 | 163 |
| -8 | 239 | 241 |
| -7 | 121 | 125 |
| -6 | 96* | 56 |
| -5 | 254 | 250 |
| -4 | 613 | 590 |
| -3 | 414 | 378 |
| -2 | 49* | -9 |
| 0 | 716 | 884 |
| 1 | 144 | 143 |
| 2 | 82 | 75 |
| 3 | 311 | 333 |
| 4 | 304 | 315 |
| 5 | 166 | 155 |
| 6 | 122 | 113 |
| 7 | 182 | 186 |
| 8 | 178 | 176 |
| 2,K,1 | | |
| -10 | 101 | 97 |
| -9 | 104 | 115 |
| -8 | 144 | 136 |
| -7 | 246 | 248 |
| -6 | 212 | 220 |
| -5 | 175 | 177 |
| -4 | 504 | 449 |
| -3 | 588 | 515 |
| -2 | 243 | 218 |
| -1 | 177 | 161 |
| 0 | 320 | 319 |
| 1 | 379 | 409 |
| 2 | 200 | 213 |
| 3 | 104 | 104 |
| 4 | 260 | 275 |
| 5 | 287 | 286 |
| 6 | 139 | 124 |
| 7 | 111 | 97 |
| 3,K,1 | | |
| -10 | 133 | 137 |
| -9 | 166 | 175 |
| -8 | 114 | 124 |
| -7 | 183 | 185 |
| -6 | 305 | 297 |
| -5 | 326 | 306 |
| -4 | 172 | 162 |
| -3 | 194 | 180 |
| -2 | 405 | 384 |
| -1 | 289 | 272 |
| 0 | 117 | 94 |
| 1 | 307 | 315 |
| 2 | 369 | 370 |
| 3 | 182 | 183 |
| 4 | 153 | 138 |
| 5 | 189 | 177 |
| 6 | 160 | 146 |
| 4,K,1 | | |
| -10 | 73 | 63 |
| -9 | 138 | 139 |
| -8 | 255 | 253 |
| -7 | 172 | 17[illegible] |
| -6 | 104* | 52 |
| -5 | 264 | 237 |
| -4 | 364 | 345 |
| -3 | 178 | 168 |
| -2 | 154 | 137 |
| -1 | 330 | 314 |
| 0 | 377 | 367 |
| 1 | 232 | 220 |
| 2 | 107 | 110 |
| 3 | 203 | 189 |
| 4 | 189 | 179 |
| 5 | 79* | 75 |
| 5,K,1 | | |
| -10 | 71 | 90 |
| -9 | 73* | 68 |
| -8 | 168 | 173 |
| -7 | 209 | 207 |
| -6 | 123 | 119 |
| -5 | 105 | 110 |
| -4 | 263 | 260 |
| -3 | 361 | 341 |
| -2 | 191 | 181 |
| -1 | 97 | 101 |
| 0 | 267 | 257 |
| 1 | 237 | 228 |
| 2 | 93* | 69 |
| 3 | 88 | 84 |
| 4 | 147 | 136 |
| 6,K,1 | | |
| -9 | 139 | 135 |
| -8 | 82 | 93 |
| -7 | 101 | 107 |
| -6 | 236 | 232 |
| -5 | 210 | 203 |
| -4 | 92 | 101 |
| -3 | 182 | 173 |
| -2 | 236 | 225 |
| -1 | 143 | 129 |
| 0 | 91* | 72 |
| 1 | 121 | 123 |
| 2 | 170 | 167 |
| 3 | 131 | 105 |
| 7,K,1 | | |
| -8 | 159 | 155 |
| -7 | 107 | 106 |
| -6 | 104 | 97 |
| -5 | 151 | 151 |
| -4 | 176 | 165 |
| -3 | 106 | 93 |
| -2 | 81* | 78 |
| -1 | 157 | 150 |
| 0 | 142 | 138 |
| 1 | 81 | 88 |
| 8,K,1 | | |
| -4 | 148 | 138 |
| -3 | 171 | 156 |
| -1,K,1 | | |
| -9 | 83 | 82 |
| -8 | 105 | 128 |
| -7 | 189 | 190 |
| -6 | 238 | 235 |
| -5 | 255 | 242 |
| -4 | 242 | 240 |
| -3 | 377 | 398 |
| -2 | 367 | 355 |
| -1 | 82 | -56 |
| 0 | 324 | 339 |
| 1 | 606 | 688 |
| 2 | 286 | 299 |
| 3 | 209 | 215 |
| 4 | 361 | 387 |
| 5 | 383 | 396 |
| 6 | 197 | 196 |
| 7 | 95* | 66 |
| 8 | 151 | 144 |
| 9 | 162 | 173 |
| -2,K,1 | | |
| -9 | 79 | 89 |
| -8 | 162 | 148 |
| -7 | 90 | 107 |
| -6 | 107* | 50 |
| -5 | 296 | 286 |
| -4 | 417 | 439 |
| -3 | 169 | 182 |
| -2 | 165 | 175 |
| 0 | 507 | 586 |
| 1 | 162 | 145 |
| 2 | 115 | -85 |
| 3 | 413 | 442 |
| 4 | 471 | 519 |
| 5 | 161 | 159 |
| 6 | 156 | 158 |
| 7 | 281 | 285 |
| 8 | 189 | 195 |
| 9 | 115 | 101 |
| -3,K,1 | | |
| -8 | 102 | 91 |
| -7 | 93 | 90 |
| -6 | 113 | 117 |
| -5 | 197 | 200 |
| -4 | 202 | 204 |
| -3 | 97 | 103 |
| -2 | 292 | 293 |
| -1 | 576 | 561 |
| 0 | 358 | 309 |
| 1 | 265 | 244 |
| 2 | 404 | 381 |
| 3 | 314 | 319 |
| 4 | 232 | 219 |
| 5 | 147 | 162 |
| 6 | 227 | 220 |
| 7 | 237 | 242 |
| 8 | 143 | 146 |
| 9 | 136 | 136 |
| 10 | 148 | 145 |
| -4,K,1 | | |
| -7 | 108 | 174 |
| -6 | 177 | 164 |
| -5 | 96 | 86 |
| -4 | 114 | 126 |
| -3 | 233 | 244 |
| -2 | 170 | 186 |
| -1 | 118 | 124 |
| 0 | 257 | 254 |
| 1 | 433 | 432 |
| 2 | 369 | 355 |
| 3 | 124 | 127 |
| 4 | 290 | 286 |
| 5 | 384 | 385 |
| 6 | 127 | 122 |
| 7 | 95* | 55 |
| 8 | 187 | 192 |
| 9 | 182 | 183 |
| 10 | 99 | 96 |
| -5,K,1 | | |
| -6 | 87 | 94 |
| -5 | 144 | 147 |
| -4 | 182 | 184 |
| -3 | 155 | 154 |
| -2 | 76 | 87 |
| -1 | 218 | 204 |
| 0 | 298 | 300 |
| 1 | 112 | 121 |
| 2 | 117 | 108 |
| 3 | 324 | 311 |
| 4 | 344 | 339 |
| 5 | 195 | 195 |
| 6 | 122 | 122 |
| 7 | 185 | 195 |
| 8 | 195 | 209 |
| 9 | 97 | 85 |
| -6,K,1 | | |
| -4 | 113 | 101 |
| -3 | 92* | 82 |
| -2 | 178 | 172 |
| -1 | 247 | 245 |
| 0 | 158 | 169 |
| 1 | 107* | 64 |
| 2 | 186 | 188 |
| 3 | 289 | 283 |
| 4 | 121 | 120 |
| 5 | 90 | 92 |
| 6 | 233 | 236 |
| 7 | 199 | 213 |
| 8 | 113 | 117 |
| 9 | 100 | 102 |
| -7,K,1 | | |
| -3 | 99 | 101 |
| -2 | 126 | 131 |
| -1 | 81 | 88 |
| 0 | 130 | 139 |
| 1 | 213 | 225 |
| 2 | 155 | 156 |
| 3 | 101 | 93 |
| 4 | 150 | 150 |
| 5 | 177 | 185 |
| 6 | 119 | 123 |
| 7 | 71 | 74 |
| 8 | 148 | 134 |
| -8,K,1 | | |
| 0 | 108 | 125 |
| 1 | 122 | 121 |
| 2 | 67 | 77 |
| 3 | 139 | 137 |
| 4 | 201 | 204 |
| 5 | 110 | 112 |
| 6 | 67* | 51 |
| 7 | 110 | 121 |
| 0,K,2 | | |
| -10 | 79 | 80 |
| -9 | 88 | 101 |
| -8 | 191 | 179 |
| -7 | 224 | 210 |
| -6 | 199 | 202 |
| -5 | 162 | 159 |
| -4 | 255 | 256 |
| -3 | 381 | 403 |
| -2 | 147 | 144 |
| -1 | 51 | 45 |
| 0 | 571 | 533 |
| 1 | 516 | 540 |
| 2 | 194 | 201 |
| 3 | 174 | 184 |
| 4 | 321 | 319 |
| 5 | 280 | 273 |
| 6 | 39 | 103 |
| 7 | 73* | 56 |
| 8 | 133 | 144 |
| 1,K,2 | | |
| -10 | 111 | 111 |
| -9 | 169 | 159 |
| -8 | 138 | 122 |
| -7 | 154 | 141 |
| -6 | 260 | 256 |
| -5 | 163 | 168 |
| -4 | 150 | 143 |
| -3 | 388 | 368 |
| -2 | 483 | 417 |
| -1 | 331 | 293 |
| 0 | 322 | 301 |
| 1 | 368 | 368 |
| 2 | 346 | 359 |
| 3 | 143 | 149 |
| 4 | 101 | 105 |
| 5 | 225 | 226 |
| 6 | 177 | 169 |
| 7 | 70 | 77 |
| 8 | 114 | 108 |
| 2,K,2 | | |
| -10 | 50* | 52 |
| -9 | 163 | 165 |
| -8 | 200 | 195 |
| -7 | 114 | 108 |
| -6 | 72* | 92 |
| -5 | 312 | 311 |
| -4 | 509 | 463 |
| -3 | 212 | 195 |
| -2 | 153 | 141 |
| -1 | 539 | 487 |
| 0 | 381 | 365 |
| 1 | 60* | 68 |
| 2 | 156 | 159 |
| 3 | 249 | 267 |
| 4 | 188 | 203 |
| 5 | 120 | 121 |
| 6 | 123 | 122 |
| 7 | 162 | 149 |
| 3,K,2 | | |
| -10 | 86 | 82 |
| -9 | 82 | 92 |
| -8 | 182 | 178 |
| -7 | 255 | 253 |
| -6 | 142 | 139 |
| -5 | 173 | 159 |
| -4 | 383 | 360 |
| -3 | 353 | 316 |
| -2 | 108 | 111 |
| -1 | 139 | 130 |
| 0 | 286 | 275 |
| 1 | 306 | 289 |
| 2 | 131 | 133 |
| 3 | 110 | 127 |
| 4 | 239 | 228 |
| 5 | 161 | 163 |
| 6 | 62 | 73 |
| 4,K,2 | | |
| -10 | 148 | 141 |
| -9 | 117 | 125 |
| -8 | 100 | 109 |
| -7 | 175 | 185 |
| -6 | 233 | 234 |
| -5 | 167 | 161 |
| -4 | 88 | 90 |
| -3 | 228 | 216 |
| -2 | 328 | 299 |
| -1 | 138 | 134 |
| 0 | 117 | 117 |
| 1 | 295 | 284 |
| 2 | 244 | 225 |
| 3 | 91 | 88 |
| 4 | 88 | 88 |
| 5 | 134 | 121 |
| 5,K,2 | | |
| -9 | 126 | 132 |
| -8 | 178 | 180 |
| -7 | 73* | 86 |
| -6 | 76* | 80 |
| -5 | 215 | 217 |
| -4 | 229 | 212 |
| -3 | 130 | 126 |
| -2 | 165 | 165 |
| -1 | 238 | 228 |
| 0 | 200 | 196 |
| 1 | 97 | 105 |
| 2 | 104 | 96 |
| 3 | 132 | 130 |
| 4 | 84 | 87 |
| 6,K,2 | | |
| -8 | 166 | 154 |
| -7 | 156 | 153 |
| -6 | 74 | 83 |
| -5 | 108 | 105 |
| -4 | 225 | 219 |
| -3 | 211 | 211 |
| -2 | 74* | 75 |
| -1 | 72 | 84 |
| 0 | 168 | 172 |
| 1 | 103 | 114 |
| 2 | 54 | 54 |
| 7,K,2 | | |
| -7 | 117 | 122 |
| -6 | 194 | 169 |
| -5 | 85 | 93 |
| -4 | 72 | 66 |
| -3 | 134 | 136 |
| -2 | 156 | 134 |
| -1 | 70 | 68 |
| 0 | 68 | 61 |
| -1,K,2 | | |
| -9 | 108 | 113 |
| -8 | 195 | 186 |
| -7 | 77* | 81 |
| -6 | 75* | 94 |
| -5 | 405 | 404 |
| -4 | 418 | 413 |
| -3 | 105 | 115 |
| -2 | 128 | 149 |
| -1 | 413 | 454 |
| 0 | 544 | 467 |
| 1 | 77 | 75 |
| 2 | 111 | 125 |
| 3 | 510 | 488 |
| 4 | 357 | 351 |
| 5 | 128 | 126 |
| 6 | 195 | 193 |
| 7 | 214 | 213 |
| 8 | 105 | 117 |
| 9 | 75 | 78 |
| -2,K,2 | | |
| -9 | 75 | 97 |
| -8 | 93 | 96 |
| -7 | 97 | 102 |
| -6 | 127 | 128 |
| -5 | 242 | 240 |
| -4 | 222 | 228 |
| -3 | 192 | 199 |
| -2 | 428 | 431 |
| -1 | 415 | 425 |
| 0 | 233 | 222 |
| 1 | 413 | 332 |
| 2 | 324 | 289 |
| 3 | 210 | 204 |
| 4 | 199 | 195 |
| 5 | 233 | 235 |
| 6 | 265 | 256 |
| 7 | 175 | 176 |
| 8 | 115 | 114 |
| 9 | 149 | 144 |
| -3,K,2 | | |
| -8 | 88 | 85 |
| -7 | 173 | 167 |
| -6 | 123 | 127 |
| -5 | 77* | 61 |
| -4 | 203 | 210 |
| -3 | 279 | 283 |
| -2 | 150 | 157 |
| -1 | 174 | 181 |
| 0 | 413 | 408 |
| 1 | 602 | 550 |
| 2 | 249 | 211 |
| 3 | 59* | 56 |
| 4 | 374 | 351 |
| 5 | 335 | 318 |
| 6 | 79* | 59 |
| 7 | 80 | 95 |
| 8 | 215 | 211 |
| 9 | 176 | 167 |
| -4,K,2 | | |
| -7 | 66 | 76 |
| -6 | 122 | 119 |
| -5 | 186 | 183 |
| -4 | 215 | 218 |
| -3 | 111 | 108 |
| -2 | 70 | 72 |
| -1 | 299 | 313 |
| 0 | 320 | 318 |
| 1 | 101 | 103 |
| 2 | 231 | 219 |
| 3 | 438 | 391 |
| 4 | 352 | 327 |
| 5 | 142 | 150 |
| 6 | 99 | 116 |
| 7 | 194 | 203 |
| 8 | 160 | 162 |
| 9 | 67 | 69 |
| -5,K,2 | | |
| -6 | 102 | 113 |
| -5 | 175 | 168 |
| -4 | 115 | 118 |
| -3 | 118 | 125 |
| -2 | 227 | 220 |
| -1 | 256 | 258 |
| 0 | 127 | 138 |
| 1 | 78 | 78 |
| 2 | 282 | 274 |
| 3 | 289 | 276 |
| 4 | 120 | 120 |
| 5 | 199 | 198 |
| 6 | 260 | 267 |
| 7 | 160 | 164 |
| 8 | 95 | 105 |
| 9 | 112 | 113 |
| -6,K,2 | | |
| -5 | 58 | 65 |
| -4 | 91 | 97 |
| -3 | 161 | 170 |
| -2 | 134 | 141 |
| -1 | 89 | 100 |
| 0 | 231 | 239 |
| 1 | 258 | 259 |
| 2 | 89 | 96 |
| 3 | 79 | 95 |
| 4 | 216 | 217 |
| 5 | 213 | 219 |
| 6 | 92 | 102 |
| 7 | 82 | 89 |
| 8 | 209 | 196 |
| -7,K,2 | | |
| -3 | 43* | 61 |
| -2 | 57* | 74 |
| -1 | 123 | 136 |
| 0 | 176 | 190 |
| 1 | 130 | 136 |
| 2 | 80 | 90 |
| 3 | 207 | 208 |
| 4 | 212 | 223 |
| 5 | 69* | 73 |
| 6 | 63* | 67 |
| 7 | 156 | 157 |
| 8 | 132 | 142 |
| -8,K,2 | | |
| -1 | 102 | 122 |
| 0 | 47* | 45 |
| 1 | 53* | 69 |
| 2 | 157 | 168 |
| 3 | 147 | 163 |
| 4 | 85 | 91 |
| 5 | 99 | 101 |
| 6 | 148 | 164 |
| 0,K,3 | | |
| -9 | 148 | 145 |
| -8 | 177 | 181 |
| -7 | 72 | 63 |
| -6 | 158 | 153 |
| -5 | 366 | 351 |
| -4 | 248 | 251 |
| -3 | 69 | 75 |
| -2 | 198 | 183 |
| -1 | 419 | 365 |
| 0 | 269 | 273 |
| 1 | 88 | 98 |
| 2 | 228 | 250 |
| 3 | 364 | 362 |
| 4 | 172 | 174 |
| 5 | 95 | 103 |
| 6 | 172 | 168 |
| 7 | 136 | 126 |
| 1,K,3 | | |
| -10 | 57 | 68 |
| -9 | 120 | 112 |
| -8 | 173 | 179 |
| -7 | 173 | 179 |
| -6 | 113 | 118 |
| -5 | 102 | 104 |
| -4 | 281 | 280 |
| -3 | 344 | 306 |
| -2 | 86 | 82 |
| -1 | 177 | 166 |
| 0 | 453 | 436 |
| 1 | 300 | 306 |
| 2 | 98 | 116 |
| 3 | 146 | 149 |
| 4 | 223 | 218 |
| 5 | 163 | 158 |
| 6 | 54 | 59 |
| 7 | 67 | 73 |
| 2,K,3 | | |
| -10 | 92 | 105 |
| -9 | 97 | 106 |
| -8 | 76 | 84 |
| -7 | 162 | 171 |
| -6 | 196 | 202 |
| -5 | 97 | 96 |
| -4 | 191 | 174 |
| -3 | 396 | 343 |
| -2 | 312 | 278 |
| -1 | 164 | 155 |
| 0 | 199 | 187 |
| 1 | 272 | 277 |
| 2 | 188 | 202 |
| 3 | 52* | 49 |
| 4 | 100 | 111 |
| 5 | 182 | 186 |
| 6 | 98 | 107 |
| 3,K,3 | | |
| -9 | 126 | 141 |
| -8 | 140 | 145 |
| -7 | 84 | 93 |
| -6 | 126 | 127 |
| -5 | 306 | 277 |
| -4 | 283 | 261 |
| -3 | 98 | 96 |
| -2 | 191 | 174 |
| -1 | 324 | 288 |
| 0 | 130 | 140 |
| 1 | 74 | 81 |
| 2 | 158 | 168 |
| 3 | 169 | 179 |
| 4 | 118 | 120 |
| 5 | 86 | 88 |
| 4,K,3 | | |
| -9 | 86 | 85 |
| -8 | 173 | 180 |
| -7 | 175 | 177 |
| -6 | 70 | 74 |
| -5 | 143 | 139 |
| -4 | 254 | 245 |
| -3 | 172 | 163 |
| -2 | 52 | 69 |
| -1 | 129 | 128 |
| 0 | 230 | 218 |
| 1 | 165 | 173 |
| 2 | 76 | 84 |
| 3 | 113 | 115 |
| 4 | 123 | 135 |
| 5,K,3 | | |
| -8 | 85 | 88 |
| -7 | 144 | 153 |
| -6 | 136 | 151 |
| -5 | 57 | 70 |
| -4 | 80 | 79 |
| -3 | 221 | 207 |
| -2 | 193 | 189 |
| -1 | 64 | 66 |
| 0 | 103 | 111 |
| 1 | 167 | 183 |
| 2 | 110 | 110 |
| 6,K,3 | | |
| -7 | 51 | 57 |
| -6 | 116 | 104 |
| -5 | 175 | 154 |
| -4 | 113 | 114 |
| -3 | 98 | 97 |
| -2 | 120 | 131 |
| -1 | 145 | 131 |
| 0 | 82 | 84 |
| -1,K,3 | | |
| -9 | 83 | 77 |
| -8 | 102 | 108 |
| -7 | 127 | 119 |
| -6 | 171 | 157 |
| -5 | 255 | 225 |
| -4 | 198 | 204 |
| -3 | 273 | 290 |
| -2 | 318 | 352 |
| -1 | 152 | 168 |
| 0 | 184 | 172 |
| 1 | 317 | 325 |
| 2 | 225 | 237 |
| 3 | 137 | 145 |
| 4 | 185 | 182 |
| 5 | 233 | 243 |
| 6 | 197 | 202 |
| 7 | 89 | 97 |
| 8 | 86 | 92 |
| -2,K,3 | | |
| -8 | 109 | 115 |
| -7 | 166 | 165 |
| -6 | 69* | 56 |
| -5 | 85 | 85 |
| -4 | 291 | 287 |
| -3 | 289 | 292 |
| -2 | 138 | 145 |
| -1 | 196 | 192 |
| 0 | 491 | 438 |
| 1 | 484 | 405 |
| 2 | 45 | 44 |
| 3 | 95 | 94 |
| 4 | 340 | 337 |
| 5 | 211 | 213 |
| 6 | 51* | 54 |
| 7 | 128 | 129 |
| 8 | 174 | 180 |
| -3,K,3 | | |
| -8 | 88 | 93 |
| -7 | 84 | 84 |
| -6 | 110 | 117 |
| -5 | 198 | 200 |
| -4 | 189 | 197 |
| -3 | 62* | 43 |
| -2 | 135 | 134 |
| -1 | 405 | 382 |
| 0 | 296 | 271 |
| 1 | 162 | 146 |
| 2 | 305 | 270 |
| 3 | 341 | 331 |
| 4 | 213 | 213 |
| 5 | 86 | 99 |
| 6 | 122 | 135 |
| 7 | 178 | 179 |
| 8 | 115 | 107 |
| -4,K,3 | | |
| -7 | 62 | 61 |
| -6 | 147 | 153 |
| -5 | 167 | 166 |
| -4 | 123 | 130 |
| -3 | 146 | 149 |
| -2 | 211 | 206 |
| -1 | 209 | 207 |
| 0 | 113 | 108 |
| 1 | 191 | 177 |
| 2 | 344 | 320 |
| 3 | 213 | 197 |
| 4 | 154 | 148 |
| 5 | 259 | 257 |
| 6 | 208 | 210 |
| 7 | 89 | 93 |
| 8 | 102 | 91 |
| -5,K,3 | | |
| -6 | 66 | 64 |
| -5 | 78 | 80 |
| -4 | 163 | 167 |
| -3 | 219 | 215 |
| -2 | 94 | 93 |
| -1 | 131 | 123 |
| 0 | 318 | 312 |
| 1 | 201 | 207 |
| 2 | 67* | 32 |
| 3 | 118 | 121 |
| 4 | 288 | 280 |
| 5 | 222 | 224 |
| 6 | 63 | 73 |
| 7 | 115 | 115 |
| 8 | 183 | 207 |
| -6,K,3 | | |
| -4 | 107 | 93 |
| -3 | 63 | 72 |
| -2 | 107 | 108 |
| -1 | 184 | 195 |
| 0 | 230 | 227 |
| 1 | 122 | 112 |
| 2 | 105 | 108 |
| 3 | 256 | 242 |
| 4 | 168 | 173 |
| 5 | 65* | 52 |
| 6 | 106 | 111 |
| 7 | 173 | 170 |
| -7,K,3 | | |
| -3 | 30* | 49 |
| -2 | 146 | 140 |
| -1 | 115 | 116 |
| 0 | 59* | 55 |
| 1 | 136 | 140 |
| 2 | 213 | 210 |
| 3 | 167 | 152 |
| 4 | 99 | 90 |
| 5 | 153 | 136 |
| 6 | 168 | 166 |
| 7 | 71 | 81 |
| -8,K,3 | | |
| 0 | 97 | 105 |
| 1 | 109 | 115 |
| 2 | 68 | 63 |
| 3 | 84 | 83 |
| 4 | 176 | 177 |
| 5 | 132 | 144 |
| 0,K,4 | | |
| -9 | 67 | 66 |
| -8 | 110 | 115 |
| -7 | 142 | 135 |
| -6 | 161 | 155 |
| -5 | 141 | 144 |
| -4 | 161 | 166 |
| -3 | 281 | 270 |
| -2 | 208 | 200 |
| -1 | 61 | 59 |
| 0 | 160 | 178 |
| 1 | 237 | 267 |
| 2 | 142 | 159 |
| 3 | 98 | 103 |
| 4 | 169 | 160 |
| 5 | 189 | 193 |
| 6 | 125 | 113 |
| 1,K,4 | | |
| -9 | 147 | 146 |
| -8 | 135 | 126 |
| -7 | 67 | 58 |
| -6 | 161 | 166 |
| -5 | 223 | 232 |
| -4 | 117 | 119 |
| -3 | 90 | 79 |
| -2 | 205 | 200 |
| -1 | 256 | 255 |
| 0 | 129 | 145 |
| 1 | 101 | 113 |
| 2 | 217 | 238 |
| 3 | 209 | 197 |
| 4 | 62 | 69 |
| 5 | 96 | 89 |
| 2,K,4 | | |
| -9 | 97 | 99 |
| -8 | 137 | 143 |
| -7 | 131 | 124 |
| -6 | 60 | 61 |
| -5 | 105 | 105 |
| -4 | 251 | 244 |
| -3 | 193 | 185 |
| -2 | 78 | 68 |
| -1 | 194 | 190 |
| 0 | 257 | 267 |
| 1 | 140 | 142 |
| 2 | 69 | 72 |
| 3 | 103 | 112 |
| 4 | 133 | 134 |
| 3,K,4 | | |
| -8 | 77 | 80 |
| -7 | 162 | 167 |
| -6 | 125 | 126 |
| -5 | 62 | 61 |
| -4 | 176 | 169 |
| -3 | 249 | 249 |
| -2 | 150 | 149 |
| -1 | 62 | 61 |
| 0 | 126 | 125 |
| 1 | 175 | 191 |
| 2 | 97 | 99 |
| 3 | 40* | 37 |
| 4,K,4 | | |
| -8 | 102 | 98 |
| -7 | 97 | 81 |
| -6 | 119 | 126 |
| -5 | 171 | 180 |
| -4 | 112 | 110 |
| -3 | 78 | 70 |
| -2 | 141 | 153 |
| -1 | 141 | 144 |
| 0 | 64 | 65 |
| 1 | 76 | 91 |
| 2 | 173 | 131 |
| 5,K,4 | | |
| -7 | 79 | 92 |
| -6 | 54 | 46 |
| -5 | 96 | 110 |
| -4 | 133 | 144 |
| -3 | 79 | 86 |
| -2 | 56 | 62 |
| -1 | 111 | 114 |
| 0 | 114 | 135 |
| -1,K,4 | | |
| -8 | 131 | 135 |
| -7 | 129 | 125 |
| -6 | 62* | 29 |
| -5 | 142 | 135 |
| -4 | 267 | 292 |
| -3 | 199 | 226 |
| -2 | 70 | 91 |
| 0 | 278 | 346 |
| 1 | 177 | 209 |
| 2 | 51* | 4 |
| 3 | 149 | 149 |
| 4 | 274 | 257 |
| 5 | 134 | 125 |
| 6 | 70 | 68 |
| -2,K,4 | | |
| -8 | 88 | 86 |
| -7 | 77 | 70 |
| -6 | 105 | 103 |
| -5 | 191 | 189 |
| -4 | 138 | 138 |
| -3 | 59 | 59 |
| -2 | 217 | 222 |
| -1 | 307 | 319 |
| 0 | 169 | 168 |
| 1 | 166 | 151 |
| 2 | 242 | 244 |
| 3 | 197 | 213 |
| 4 | 104 | 107 |
| 5 | 90 | 88 |
| 6 | 145 | 147 |
| 7 | 125 | 128 |
| -3,K,4 | | |
| -7 | 102 | 99 |
| -6 | 142 | 141 |
| -5 | 123 | 122 |
| -4 | 121 | 126 |
| -3 | 160 | 154 |
| -2 | 176 | 173 |
| -1 | 144 | 132 |
| 0 | 154 | 132 |
| 1 | 364 | 273 |
| 2 | 297 | 258 |
| 3 | 102 | 104 |
| 4 | 150 | 155 |
| 5 | 246 | 227 |
| 6 | 113 | 124 |
| 7 | 60 | 52 |
| -4,K,4 | | |
| -6 | 73 | 60 |
| -5 | 99 | 101 |
| -4 | 224 | 227 |
| -3 | 192 | 181 |
| -2 | 38* | 22 |
| -1 | 150 | 148 |
| 0 | 336 | 298 |
| 1 | 180 | 140 |
| 2 | 57* | 28 |
| 3 | 188 | 168 |
| 4 | 299 | 285 |
| 5 | 172 | 166 |
| 6 | 50 | 51 |
| 7 | 138 | 126 |
| -5,K,4 | | |
| -5 | 121 | 113 |
| -4 | 97 | 100 |
| -3 | 95 | 94 |
| -2 | 134 | 138 |
| -1 | 233 | 218 |
| 0 | 203 | 187 |
| 1 | 81 | 70 |
| 2 | 155 | 137 |
| 3 | 247 | 210 |
| 4 | 117 | 109 |
| 5 | 80 | 79 |
| 6 | 164 | 148 |
| 7 | 156 | 147 |
| -6,K,4 | | |
| -4 | 26* | 33 |
| -3 | 84 | 86 |
| -2 | 157 | 156 |
| -1 | 89 | 94 |
| 0 | 102 | 99 |
| 1 | 203 | 197 |
| 2 | 205 | 190 |
| 3 | 110 | 98 |
| 4 | 96 | 87 |
| 5 | 158 | 161 |
| 6 | 141 | 132 |
| -7,K,4 | | |
| -1 | 89 | 85 |
| 0 | 142 | 146 |
| 1 | 119 | 117 |
| 2 | 50 | 46 |
| 3 | 132 | 133 |
| 4 | 204 | 211 |
| 5 | 131 | 110 |
| 0,K,5 | | |
| 0 | 220 | 221 |
| 1,K,5 | | |
| 0 | 170 | 169 |
| 2,K,5 | | |
| 0 | 74 | 70 |
| 3,K,5 | | |
| 0 | 144 | 128 |
| -1,K,5 | | |
| 0 | 83 | 85 |
| -2,K,5 | | |
| 0 | 163 | 159 |
| -3,K,5 | | |
| 0 | 262 | 234 |
| -4,K,5 | | |
| 0 | 107 | 103 |
| -5,K,5 | | |
| 0 | 125 | 134 |
| -6,K,5 | | |
| 0 | 171 | 176 |
| 0,K,6 | | |
| 0 | 51 | 47 |
| -1,K,6 | | |
| 0 | 143 | 154 |
| -2,K,6 | | |
| 0 | 140 | 152 |
| -3,K,6 | | |
| 0 | 59 | 51 |
| -4,K,6 | | |
| 0 | 119 | 136 |

[a] Columns are k index, $10F_o$, $10F_c$. Unobserved reflections are marked by an asterisk.

structure factor calculation is the same as that obtained when the calculated hydrogen positions are used.

## Description and Discussion of the Structure

The shortest Pd–Cl distance present in the structure is 4.180 ± 0.002 A. This distance is much longer than the shortest nonbonding Pd–Cl distance of 3.85 A between chains in the crystal structure of $PdCl_2$.[11] Therefore, it appears that there is no covalent bonding between palladium and chlorine and it seems proper to describe the crystal structure of $Pd(en)_2Cl_2$ as consisting of discrete $[Pd(en)_2]^{2+}$ and $Cl^-$ ions. These ions are bound together in sheets parallel to (010) by a network of $NH\cdots Cl$ hydrogen bonds. These sheets have only van der Waals forces binding them together in the crystal. The closest approach distances between the sheets are 3.949 and 3.933 A between carbon atoms on adjacent molecules and 3.867 A between a carbon atom and a nitrogen atom on adjacent molecules. Taking the van der Waals radius of a methylene group as 2.0 A,[12] the carbon–carbon approach distances seem quite reasonable. The orthogonal projection of one of these sheets onto (010) is shown in Figure 2.

An orthogonal projection of the $[Pd(en)_2]^{2+}$ ion onto a plane parallel to the coordination plane is shown in Figure 3. The molecular symmetry required by the space group is $\bar{1}$. Accordingly, the ligands are arranged about the palladium atom in a planar configuration. The carbon atoms of the ethylenediamine are in the *gauche* conformation as has been found in all structures so far reported in which ethylenediamine is used as a ligand. The atom C(1) is at a distance of 0.33 A above the N(1)–Pd–N(2) plane while atom C(2) is 0.39 A below this plane. These distances are not considered to be significantly different. The N(1)–Pd–N(2) plane makes an angle of 28.3° with the C(1)–Pd–C(2) plane.

Interatomic distances and angles are given in Table IV. The standard deviations given were calculated using the program ORFFE[13] as modified for inclusion in the Crystal Structures Calculations system[9] and therefore include the effects of correlation. For comparison with this structure, Table V gives interatomic distances and angles of interest in some other structures. Using the criteria suggested by Jeffrey and Cruickshank,[14] none of the distances or angles can be considered to be significantly different ($t = 3$), although

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[11] A. F. Wells, *Z. Krist.*, **100A**, 189 (1938).

[12] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

[13] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

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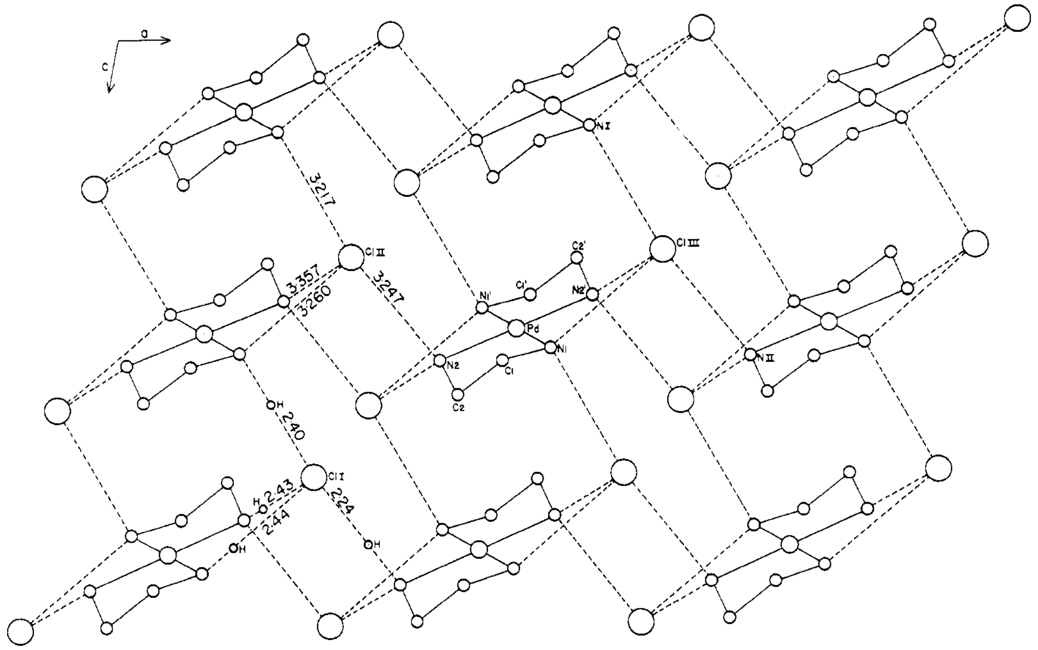

Figure 2.—Orthogonal projection of structure onto (010). The hydrogen atoms around Cl(I) are depicted schematically only.

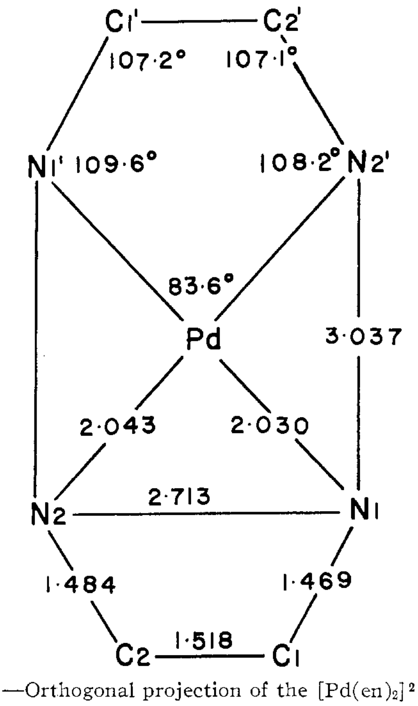

Figure 3.—Orthogonal projection of the $[Pd(en)_2]^{2+}$ ion onto the Pd–N(1)–N(2) plane.

Table IV

Interatomic Distances and Angles[a]

| Distance, A | | Angle, deg | |
|---|---|---|---|
| Pd–N(1) | 2.030 (6) | N(1)–Pd–N(2) | 83.6 (3) |
| Pd–N(2) | 2.043 (7) | Pd–N(1)–C(1) | 109.6 (5) |
| N(1)–C(1) | 1.469 (11) | Pd–N(2)–C(2) | 108.2 (5) |
| N(2)–C(2) | 1.484 (11) | N(1)–C(1)–C(2) | 107.2 (7) |
| C(1)–C(2) | 1.518 (13) | N(2)–C(2)–C(1) | 107.1 (7) |
| N(1)–N(2) | 2.713 (10) | | |
| N(1)–N(2)'[b] | 3.037 (10) | | |

[a] Standard deviations in the least significant digits are shown in parentheses. [b] N(2)' is related to N(2) by inversion through the center of symmetry.

the N–N distances listed show a variation that could possibly be significant. Lingafelter and Braun[15] have found that among several acetylacetone–metal chelate compounds the oxygen–oxygen distance varies quite significantly, and it would therefore be reasonable to expect some variation of the nitrogen–nitrogen distance among the ethylenediamine–metal chelates, but, until more structures of this type are accurately determined, no definitive statement can be made concerning this.

The Pd–N distances of 2.030 ± 0.006 and 2.043 ± 0.007 A are in good agreement with the Pd–N distances of 2.031 ± 0.002 A in bis(N-isopropyl-3-ethylsalicylaldiminato)palladium(II),[16] 2.022 ± 0.007 A in bis-(2,2'-dipyridyliminato)palladium(II),[17] and 2.032 ± 0.003 A in the tetragonal form of bis(N-isopropyl-3-methylsalicylaldiminato)palladium(II).[18]

The chloride ions are surrounded by four hydrogen atoms at distances of 2.44, 2.43, 2.40, and 2.24 A. These distances are depicted around Cl(I) in Figure 2. It should be noted here that any data given which involve hydrogen atom parameters are only for the purpose of establishing a hydrogen-bonding scheme and no great accuracy should be attached to the values since the hydrogen positions were determined from only one difference synthesis and were not refined. These H···Cl distances are all significantly smaller than the sum of the van der Waals radii of chlorine and hydrogen (1.8 + 1.2 = 3.0 A) as given by Pauling.[12] The distances from the chloride ion to the nitrogen atoms to which these hydrogen atoms are attached are shown around Cl(II) in Figure 2. Pimentel and Mc-

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(15) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).

(16) R. L. Braun and E. C. Lingafelter, to be published.

(17) H. C. Freeman and M. R. Snow, *Acta Cryst.*, **18**, 843 (1965).

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TABLE V

COMPARISON OF BOND LENGTHS AND ANGLES

| Compd | Ref | N–N,[a] A | N–C, A | C–C, A | ∠N–M–N, deg | ∠M–N–C, deg | ∠N–C–C, deg |
|---|---|---|---|---|---|---|---|
| $Ni(en)_3(NO_3)_2$ | *b* | 2.790 (25) | 1.500 (25) | 1.498 (28) | 82.3 (10) | 109.7 (12) | 111.1 (23) |
| $Cu(en)_2(NO_3)_2$ | *c* | 2.772 | 1.487 (25) | 1.545 (27) | 86.2 | 109.1 | 109.6 |
| | | | 1.476 (25) | | | 108.5 | 110.6 |
| $Cu(en)_2(SCN)_2$ | *d* | 2.70 (3) | 1.46 (3) | 1.56 (4) | 84.8 | 110.5 | 109.4 |
| | | | 1.49 (3) | | | 108.6 | 104.7 |
| $Pd(en)_2Cl_2$ | *e* | 2.713 (10) | 1.469 (11) | 1.518 (13) | 83.6 (3) | 108.2 (5) | 107.2 (7) |
| | | | 1.484 (11) | | | 109.6 (5) | 107.1 (7) |

[a] Within a chelate ring. [b] L. N. Swink and M. Atoji, *Acta Cryst.*, **13,** 639 (1960). [c] Y. Komiyama and E. C. Lingafelter, *ibid.*, **17,** 1145 (1964). [d] B. W. Brown and E. C. Lingafelter, *ibid.*, **17,** 254 (1964). [e] This investigation.

TABLE VI

PERTINENT DATA INVOLVED IN THE HYDROGEN-BONDING SCHEME[a]

Distances of the Hydrogen Atoms from the Line Joining the Chloride Ion and the Nitrogen Atoms

| Atoms defining line | Distance of hydrogen from the line, A |
|---|---|
| N(1)–Cl(III) | 0.16 |
| N(2)′–Cl(III) | 0.36 |
| N(I)–Cl(III) | 0.35 |
| N(II)–Cl(III) | 0.03 |

Angles Involved in the Hydrogen-Bonding Geometry

| | |
|---|---|
| N(1)–Cl(III)–N(2)′ | 54.6° |
| N(1)–Cl(III)–N(I) | 100.9° |
| N(2)′–Cl(III)–N(I) | 87.6° |
| N(I)–Cl(III)–N(II) | 153.4° |
| N(2)′–Cl(III)–N(II) | 76.1° |
| N(1)–Cl(III)–N(II) | 86.8° |

[a] The lettering refers to the atoms surrounding Cl(III) in Figure 2.

Clellan[19] list N···Cl hydrogen-bonded distances ranging from 2.91 to 3.41 A. These distances in the present structure fall quite nicely within this range. Table VI gives the distances of the hydrogen atoms from the lines joining the chloride ion and the nitrogen atoms.

It can thus be seen that the positions of the hydrogen atoms indicate that there is hydrogen bonding taking place between the chloride ions and the nitrogen atoms. Some pertinent angles concerning the geometry of the nitrogen atoms surrounding the chloride ion are also given in Table VI.

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[19] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco and London, 1960, p 290.

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# Crystal Structures and Multiple Bonding in *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ and *trans*-$Pt[P(C_2H_5)_3]_2Br_2$

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The crystal structures of the isomorphous pair *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ and *trans*-$Pt[P(C_2H_5)_3]_2Br_2$ have been determined from counter data by two- and three-dimensional single-crystal X-ray techniques, respectively. The structures consist of discrete molecules with the platinum, phosphorus, and halogen atoms in essentially a square-planar arrangement. Only van der Waals interactions exist between molecules. The Pt–P bond lengths were found to be 2.300 ± 0.019 and 2.315 ± 0.004 A in the chloride and bromide, respectively. A Pt–P distance of 2.41 A would be expected from the sum of the single-bond covalent radii. The Pt–Cl and Pt–Br distances were found to be normal single bonds at 2.294 ± 0.09 and 2.428 ± 0.002 A, respectively. Within experimental error, the P–C distances were observed to be normal single bonds, and the Pt–P–C angles tetrahedral.

## Introduction

The influence of $\pi$ bonding on *cis–trans* isomerization and the *trans*-directing effect has been discussed for some time.[3–7] In Pt(II) complexes the usually nonbonding $5d_{xz}$, $5d_{yz}$ filled metal orbitals can interact with $\pi$ orbitals of appropriate symmetry. With trialkylphosphine ligands these are the empty phosphorus

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