**The Nitrate Ion.**—The nitrate ions lie on $C_2(z)$ sites at $z \sim {}^1/_8$ in the crystal and are oriented nearly parallel to the (100) and (010) planes. One N–O bond of each anion is directed along $z$. There are four ions in the primitive cell. The two unique bond lengths determined in the structure study, 1.230 (6) and 1.238 (6) Å, agree well with the value of 1.241 (2) Å found in $NaNO_3$.[24] Bond angles in the anion are within three standard deviations of 120°. The $NO_3^-$ ion has four modes of vibration (Figure 7), the symmetric ($a_1'$) and asymmetric ($e'$) stretching modes, the in-plane bending mode ($e'$), and the out-of-plane deformation ($a_2''$).

The symmetric stretching mode and the in-plane bending mode can be readily assigned to bands at 1052 $cm^{-1}$ (Raman) and about 713 $cm^{-1}$ (Raman and ir), respectively. The out-of-plane deformation is attributed to an infrared band at either 824 or 829 $cm^{-1}$; the other probably originates in the nitro group. The asymmetric stretching mode can be assigned to the Raman ($A_1$) band at 1402 $cm^{-1}$. Other bands in this region may arise from either the nitrate ion or the nitro ligand.

Bands in the low-frequency range may originate in the $NO_2$ bending and twisting modes, skeletal bending modes of the complex ions, and lattice modes. Because of the complexity of this part of the spectrum, assignment of bands to vibrational modes was not attempted.

**Nonbonded Interactions.**—Packing in this structure appears to be based on a combination of weak ionic attractions and disordered N–H···O interactions (see Table VII). Consider first the cations and their 2:1 stoichiometry. In Figure 8 it can be seen that the two nitrotriamminepalladium ions pack along the [001] direction so that their $NO_2$ groups occupy vacant axial octahedral sites around Pd(1), resulting in a monopole–dipole interaction and a coordination number of 6. Such higher coordination numbers for Pd(II) are rare but not unknown.[25] The Pd(1)–O(1) distance is 3.175 Å. The $NO_2$ oxygen atoms show a large thermal motion in the (110) plane suggesting a rotational disorder, constrained perhaps by the surrounding negatively charged $NO_3^-$ anions. The axial octahedral sites for Pd(2) are occupied by $NH_3$ groups of neighboring nitrotriamminepalladium ions with the N(2)–Pd(2) distance of 3.393 Å suggesting a very weak ionic interaction.

Evidence for a second type of weak interaction is apparent in Table VII where four close approaches to nitrate oxygen atoms are listed for each of the three unique $NH_3$ groups. The geometry of the approaches, shown with dashed lines in Figure 8, places the $NH_3$ hydrogen atoms in positions suitable for N–H···O interactions. However, only three hydrogens are available for each set of four approaches, and these atoms would be disordered in any such system. In the case of the hydrogens of N(3) the space group *requires* disorder. The observed N–O distances range from 2.993 to 3.287 Å for these approaches, considerably shorter than the distance of approximately 3.6 Å expected in the absence of an interaction but longer than the observed values of 2.8 Å for N–H···O bonds in other structures.[26]

[24] P. Cherin, W. C. Hamilton, and B. Post, *Acta Crystallogr.*, **23**, 455 (1967).

[25] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 1023.

[26] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

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# The Crystal Structure of Dichlorobis(1-methyltetrazole)zinc(II)

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The crystal structure of dichlorobis(1-methyltetrazole)zinc(II), $Zn(C_2N_4H_4)_2Cl_2$, has been determined at room temperature using a three-dimensional set of intensities obtained by film methods. A total of 1278 independent present reflections were collected. The unit cell is monoclinic with the following dimensions (temperature 22°): $a = 9.455 \pm 0.002$ Å, $b = 13.595 \pm 0.008$ Å, $c = 9.677 \pm 0.002$ Å; $\beta = 104.33 \pm 0.02°$; space group $P2_1/c$; $Z = 4$; $d_m = 1.66 \pm 0.02$ g $cm^{-3}$, $d_c = 1.68$ g $cm^{-3}$. The structure was refined by least-squares methods to a Hamilton's $R$ factor of 9.7%. The coordinating ligands form a distorted tetrahedron about the zinc atom with the zinc atom being essentially planar with the tetrazole rings. The site of coordination to the tetrazole ring is the 4 position of the ring. The angles and average distances found were as follows: Zn–Cl, 2.202 ± 0.003 Å; Zn–N, 2.05 ± 0.01 Å; Cl–Zn–Cl, 118.3 ± 0.2°; N–Zn–N, 98.9 ± 0.3°.

## Introduction

Various derivatives of tetrazole are able to form complexes with many metal ions.[1,2] Gilbert and Brubaker[3] reported the formation of various metal–tetrazole complexes with the general formula $M^{II}TzCl_2$ where M = Zn, Co, Pt, or Ni and Tz = 1-methyl-, 1-cyclohexyl-, or 1-phenyltetrazole. However, neither the nature of the metal–tetrazole interaction nor the coordination site of the tetrazole ring could be determined from the available experimental data. A similar difficulty in determining the nature of the interaction between vari-

[1] F. R. Benson, *Heterocycl. Compounds*, **8**, 10 (1967).

[2] D. M. Bowers and A. I. Popov, *Inorg. Chem.*, **7**, 1594 (1968).

[3] G. L. Gilbert and C. H. Brubaker, Jr., *ibid.*, **2**, 1216 (1963).

ous first-row transition metal halides and pentamethylenetetrazole was found by Bowers and Popov.[2]

A crystallographic investigation[4] of iodopentamethylenetetrazolium monochloride (PMTICl) revealed that the tetrazole ring acts as a unidentate ligand. The site of coordination of PMTICl was at position 4. Additional coordination sites exist on the tetrazole ring, and it has been suggested[2] that apparent polymeric metal–tetrazole complexes may be explained by assuming that tetrazole functions as a bidentate ligand.

The coordination in PMTICl was explained on the basis of a donor–acceptor model with the nitrogen atom at position 4 of the ring acting as a donor through a $\sigma$-type bond which is planar with the ring.[4] Imidazole[5–7] and other ligands[8,9] containing a pyridine type nitrogen atom exhibit similar coordination through a $\sigma$ bond coplanar with the ring. Bonding occurring at a pyrrole-type nitrogen atom (>N–H) would be expected to lack coplanarity with the ring.[7]

The fact that tetrazoles bear a formal resemblance to cyclopentadiene[3] suggests that a sandwich compound analogous to ferrocene[10] may form.

In view of the several modes of coordination which tetrazole may assume in the complexes, a crystal structure analysis was undertaken. The determination of the type of metal–tetrazole bond and the site on the tetrazole ring to which coordination occurs were anticipated as the results of this study. The zinc chloride–1-methyltetrazole complex was selected for analysis because it formed crystals suitable for an X-ray study and because it was deemed typical of the several complexes prepared.[11]

## Experimental Section

Dichlorobis(1-methyltetrazole)zinc(II) (ZCTZ), $Zn(C_2N_4H_4)_2Cl_2$, formed colorless monoclinic prisms elongated along *b*. Crystals suitable for structure analysis were obtained by slowly cooling a saturated solution of ZCTZ in ethyl alcohol. Reciprocal cell dimensions and errors were calculated by a least-squares treatment of back-reflection Weissenberg (Cu K$\alpha$, $\lambda_1$ 1.54051 Å, $\lambda_2$ 1.54433 Å) single-crystal diagrams: $a = 9.455$ (2) Å, $b = 13.595$ (8) Å, $c = 9.677$ (2) Å, $\beta = 104.33$ (2)° (temperature 22°).

The equiinclination Weissenberg photographs (Cu K$\alpha$) (*h*0*l*), (*h*1*l*), and (*h*2*l*) showed that (*hkl*) were present in all orders while (0*k*0), $k = 2n + 1$, and (*h*0*l*), $l = 2n + 1$, were absent. The systematic extinctions are consistent with the unique space group $P2_1/c$.

The density calculated from X-ray data is 1.68 g cm$^{-3}$ ($Z = 4$). A measured density of 1.66 (2) g cm$^{-3}$ was obtained by the flotation method ($ZnCl_2$(aq)).

Three-dimensional data were collected at room temperature. Eight layers, (*h*0*l*)–(*h*7*l*), were collected by multifilm nonintegrated Weissenberg equiinclination techniques (Cu K$\alpha$, Ni filter) from an elongated diamond-shaped platelet (major axis of the diamond along *b** was 0.90 mm; minor axis of the diamond along *c** was 0.70 mm; the platelet was 0.10 mm thick with the *a* axis normal to the platelet). The intensity of a reflection was obtained by visual comparison to a calibrated intensity scale prepared from the same crystal. Each reflection which was judged to be above the minimum observable intensity was estimated several times from which the average intensity, $I_h$, and the per cent standard deviation $(\%s_I)_h$ were calculated. A plot of $(\%s_I)_h$ *vs.* $I_h$ was prepared and fitted by the function $(\%s_I)_h = 2.5((\log 3.3I_h) - 4.0)^2 + 6.7$. The weight used during the least-squares refinement is given by $w = 1/s_F^2 = [F(\%s_I)_h/2]^{-2}$. The effect of the weighting procedure was to "smooth" the weights, giving a particular reflection an uncertainty of the same magnitude as the other reflections of approximately the same intensity, and, also, to reduce the importance of the visual data relative to the precession data described below. The Weissenberg data were corrected for absorption ($\mu = 69.01$ cm$^{-1}$, Cu K$\alpha$) using the method of Alberti and Gottardi.[12] The average value of $e^{-\mu D}$ ranged from 0.18 to 0.54.

Eleven layers of integrated precession data (Mo K$\alpha$, Zr filter, $\lambda$ 0.7107 Å) were collected from two crystals: (a) (0*kl*)–(3*kl*), (*hk*0)–(*hk*3), mounted along *b** (0.29 × 0.38 × 0.38 mm [$a \times b \times c$]); (b) (*h*0*l*)–(h2*l*), mounted along *a** (0.31 × 0.33 × 0.37 mm [$a \times b \times c$]). Two exposures per layer were used to maintain the optical density within linear range. A densitometer was used to obtain the intensity of each reflection. The values of the intensity of a reflection were averaged and weights calculated as above except no "smoothing" was employed. No correction for absorption was applied to the precession data ($\mu = 25.16$ cm$^{-1}$, Mo K$\alpha$). A maximum error of 5% is introduced by neglecting absorption.

All told, 3321 reflections were tabulated representing 2036 independent reflections of which 1278 were considered to be present and 758 were considered to be absent. Individual scale parameters were refined for all data sets. Common reflections between data sets obtained with Mo radiation were averaged just prior to the last two cycles of refinement when $R_{Hx} = 0.11$. Common reflections between the Cu and Mo radiation data sets were not averaged because the dispersion corrections are different.

## Structure Determination and Refinement

The atom scattering factors and dispersion corrections used in the structure factor calculations were taken from ref 13. The data were corrected for Lorentz and polarization factors. Both real and imaginary dispersion corrections were applied for Zn and Cl during the latter stages of refinement. The full-matrix least-squares refinement was carried out using a locally written program for the IBM 360 computer. The least-squares program calculates the structure factor using a complex atom scattering factor (due to the dispersion terms), and the data are flagged to denote whether they were obtained with Cu or Mo radiation, since the dispersion terms differ. The progress of the refinement was followed using Hamilton's $R$ factor ($\Delta F = F_o - F_c$)

$$R_H = \left[\frac{\sum w(\Delta F)^2}{\sum w(F_o)^2}\right]^{1/2}$$

The function minimized was $\Sigma w(\Delta F)^2$. During refinement, any intensity below the minimum observable intensity was given $w = 0$ unless $|F_o| < |F_c|$ in which case it was given $w = 1$.

The structure of ZCTZ was determined in two steps. The first step used a data set consisting of the Weissenberg data reported here, and several layers of precession

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(10) T. J. Kealy and P. L. Paulson, *Nature (London)*, **168**, 1039 (1951).

(11) C. H. Brubaker, private communication.

(12) A. Alberti and G. Gottardi, *Acta Crystallogr.*, **21**, 833 (1966).

(13) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1959, pp 202, 214, 215.

TABLE I

FRACTIONAL ATOMIC COORDINATES AND MEAN-SQUARE AMPLITUDE TENSORS

| | $x^a$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Zn | 1930 (2) | 787 (1) | 3804 (1) | 45 (1) | 70 (1) | 31 (1) | −1 (1) | 6 (1) | 1 (1) |
| Cl(1) | 1992 (4) | −643 (3) | 2744 (3) | 82 (2) | 68 (3) | 46 (2) | 8 (2) | 19 (2) | −4 (2) |
| Cl(2) | 5 (4) | 1730 (3) | 3051 (4) | 55 (2) | 85 (3) | 97 (3) | 22 (2) | 6 (2) | 10 (3) |
| N(1) | 2186 (14) | 644 (10) | 8122 (11) | 71 (7) | 76 (9) | 31 (5) | −30 (8) | 5 (5) | 7 (6) |
| N(2) | 3285 (16) | 7 (11) | 8054 (12) | 84 (9) | 109 (11) | 39 (7) | −12 (9) | −12 (7) | 9 (7) |
| N(3) | 3308 (13) | 17 (10) | 6707 (12) | 71 (8) | 79 (88) | 57 (4) | 32 (7) | 21 (6) | 22 (7) |
| N(4) | 2251 (10) | 618 (8) | 5953 (10) | 51 (6) | 50 (7) | 41 (5) | 20 (6) | 13 (5) | 0 (5) |
| C(5) | 1565 (15) | 948 (10) | 6867 (13) | 70 (8) | 66 (11) | 47 (7) | 12 (8) | 25 (6) | −15 (7) |
| C(6) | 1896 (18) | 793 (13) | 9508 (15) | 122 (13) | 96 (13) | 53 (8) | 13 (12) | 26 (8) | −5 (10) |
| N′(1) | 5823 (11) | 2326 (7) | 4240 (9) | 49 (6) | 55 (7) | 26 (5) | 10 (6) | 8 (4) | −9 (5) |
| N′(2) | 5091 (13) | 2564 (10) | 2934 (12) | 62 (7) | 121 (12) | 54 (7) | −35 (8) | 12 (7) | 9 (7) |
| N′(3) | 3878 (13) | 2014 (9) | 2689 (11) | 65 (7) | 86 (10) | 52 (7) | −7 (8) | −10 (6) | 7 (7) |
| N′(4) | 3793 (10) | 1579 (7) | 3791 (8) | 61 (6) | 48 (7) | 18 (4) | −10 (6) | 15 (4) | 1 (4) |
| C′(5) | 5006 (11) | 1705 (9) | 4752 (11) | 37 (5) | 38 (8) | 31 (5) | −33 (6) | 1 (5) | 2 (5) |
| C′(6) | 7307 (14) | 2695 (10) | 4973 (13) | 51 (7) | 93 (12) | 43 (7) | −21 (8) | −6 (6) | 16 (8) |
| H(1)[b] | 722 | 798 | 9278 | | | | | | |
| H(2) | 2383 | 1537 | 7618 | | | | | | |
| H(3) | 2456 | 271 | 7544 | | | | | | |
| H(4) | 812 | 1428 | 9188 | | | | | | |
| H′(1) | 7118 | 3349 | 5564 | | | | | | |
| H′(2) | 7625 | 3046 | 4085 | | | | | | |
| H′(3) | 8086 | 2202 | 5492 | | | | | | |
| H′(4) | 5293 | 1353 | 5762 | | | | | | |

[a] Fractional coordinates with standard deviations in parentheses ($\times 10^4$). The $U_{ij}$'s (Å$^2$) are given together with standard deviations in parentheses ($\times 10^3$) and defined such that the atomic temperature factor is given by $\exp[-2\pi^2(h^2a^*U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. [b] Methyl protons are designated 1–3; H(4) is next to C(5); the isotropic temperature factor $B$ = 4.5 was assigned to all protons.

data which are not reported. These data were initially scaled by means of a Wilson plot, and the initial positions of all nonhydrogen atoms were determined by the "heavy-atom method." The initial positions gave $R_H$ = 34% which was reduced to $R_H$ = 15% at the conclusion of refinement with individual isotropic temperature factors. Refinement proceeded with Zn, Cl(1), and Cl(2) anisotropic to $R_H$ = 14% and with all atoms anisotropic to $R_H$ = 13%.

Because the final structure of step one showed corresponding bond distances in the tetrazole rings which did not agree within experimental limits of error, a second step in the refinement was performed. The data used in step two consisted of the Weissenberg data of step one plus the integrated precession data reported here. Using the atom parameters of the previous step, $R_H$ = 13%. During refinement, a few reflections were assigned $w = 0$ if they were near a region of high background or if they were on a radiation streak from another reflection. Since these were mostly low-angle reflections, their removal lessened the need for extinction corrections as well.

Since the carbon atom of the tetrazole ring must appear at either position 2 or 5 (Figure 1), an attempt was made to determine the position of the carbon atom. In both steps of refinement, models having a carbon atom at position 2 and a nitrogen atom at position 5 (and *vice versa*) were tested. An example of one test will indicate the type of results obtained. Initially, all ring atoms were treated as nitrogen atoms and refined with isotropic temperature factors ($R_H$ = 0.15). After designating C(5) and C′(5) as C atoms, the $B$ value changed from 5.9 to 4.4 and from 5.9 to 4.4 for these two atoms.

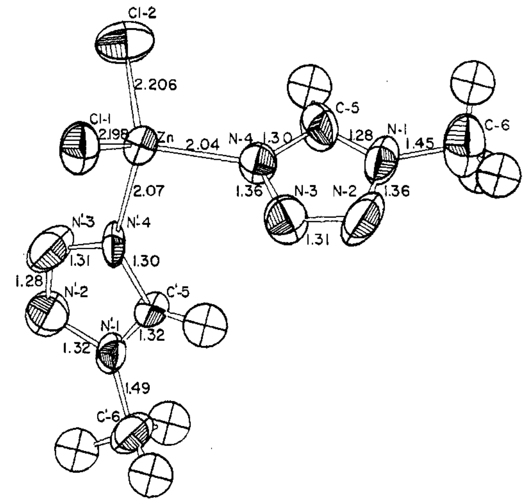

Figure 1.—The structure of a molecular unit of dichlorobis(1-methyltetrazole)zinc(II). The drawing was prepared by ORTEP: C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program. Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

The $B$ values for N(2) and N′(2) changed from 6.4 to 6.2 and from 5.1 to 4.5 ($R_H$ = 0.13). After designating the atoms in the reversed fashion, N(5) and N′(5) and C(2) and C′(2), the $B$ values changed from 5.9 to 6.1 for N(5), from 5.9 to 6.4 for N′(5), from 6.4 to 3.9 for C(2), and from 5.1 to 2.7 for C′(2), ($R_H$ = 0.14). Since the changes in $B$ in the second case appeared to be attempts to compensate for incorrect choices of the atom type, the correct atom assignment was assumed to be C(5), C′(5), N(2), and N′(2).

This assignment is consistent with the assignment

## TABLE II

### CALCULATED AND OBSERVED STRUCTURE FACTORS FOR DICHLOROBIS(1-METHYLTETRAZOLE)ZINC(II)[a]

```
  L  FO  FC WT
   H= 0,K=  0
  2 605 749  2+
  4 256 251 58
  4 190 218 10+
  6  95  87 15+
  8 151 191 15
  8 157 157 10+
 10 160 147 14
 10 142 163 11+
 12  76 116 23+
   H= 0,K=  1
  1 827 751  2
  2 995 911  7
  2 750 877  1+
  3 728 751  9
  3 645 721  2+
  4  50  66 24+
  5 319 325 11
  5 284 292  7+
  7  55  60 19+
  9 262 274  5
  9 274 286  7+
 10  79  84 16+
 11  56  94 21+
   H= 0,K=  2
  0 369 380  1
  1 314 274  6
  1 242 238  8+
  2 309 309 50
  2 302 310  6+
  3 582 525 24
  3 411 497  4+
  4 410 383 17
  4 361 368  5+
  5 389 355 40
  5 303 338  6+
  7 232 251 20
  7 239 218  8+
  8 101  85 13+
  9 121 132 12+
 11  90 121 17+
   H= 0,K=  3
  1 291 270 49
  1 254 272  7+
  2 337 314 13
  2 242 260  8+
  3 219 214 32
  3 224 216  9+
  4 229 237 20
  4 209 236  9+
  5 166 185 21
  5 181 185 10+
  6 480 527  4+
  6 581 567  8
  7  69  60 17+
  8 131 134 12+
  9  54   4 18+
 10  66  92 18+
   H= 0,K=  4
  1 638 710 13
  1 586 733  2+
  2 112  97 16+
  3 648 595  5
  3 504 579  3+
  4 274 284 12
  4 254 271  8+
  5 411 423  4
  5 369 402  5+
  7 209 263 11
  7 207 232  9+
  8 130 129 12+
  9  97 109 14+
   H= 0,K=  5
  1 189 167 10+
  2 147 166 14
  2 152 148 13+
  3 208 216 22
  3 194 202 10+
  4 129 153 13+
  5 177 248  3
  5 197 220 10+
  6 188 207 10+
  7  87  86 15+
  8  64  48 17+
  9 149 177 11+
 11  44  25 26+
   H= 0,K=  6
  0 526 573  4
  1  84  54 18+
  2  61  42 21+
  3 116  96 14+
  4 247 275 11
  4 225 230  9+
  5  53  50 20+
  6 200 217  8
  6 190 213  9+
  8 151 153 11+
   H= 0,K=  7
  1 217 258 33
  1 223 237  9+
  2  47  28 23+
  3 265 273 54
  3 225 250  9+
  4 140 157 14
  4 153 158 11+
  5 209 230 13
  5 186 200 10+
  6  94  86 14+
  7  52  63 18+
  8  77  73 15+
  9 157 175 11+
 10  42  19 25+
   H= 0,K=  8
  0 484 545  3
  2 122 139 22
  3 172 174 10
   H= 0,K=  9
  1 147 169 32
  2 214 241 35
  3 148 101 31
  6 186 161  8
   H= 0,K= 10
  1 123 114 28
  3 181 181  8
  5 168 166 10
   H= 0,K= 11
  2 172 189 43
   H= 0,K= 12
  0 327 297 43
   H= 0,K= 14
  0 175  98 20
   H= 1,K=  0
  0 157 123 12+
  2 582 482 24
  2 448 428  3+
  4 361 335 43
  4 336 330  6+
 -4  50  50 25+
  6 159 168 24
  6 134 114 12+
 -6 228 220 30
 -6 192 174 10+
  8 120 115  9
  8 141 126 11+
 -8 212 217 33
 -8 198 199  9+
 10 204 263  9+
-10 212 239  8
-10 236 260  8+
   H= 1,K=  1
  0 272 366  6+
  1 294 257  6+
 -1 158 129 13+
  2 106  95 18+
 -2 177 181 11+
  3 190 180  8
  3 222 196  9+

  L  FO  FC WT
 -3 440 445  4+
  4 276 258 30
  4 244 244  8+
 -4 700 582 20
 -4 516 572  3+
 -5  83  91 18+
  6  47  45 21+
 -6 141 115  3
 -6 102 100 15+
  7 449 452 31
  7 408 433  5+
 -7 429 435 32
 -7 399 397  5+
  8  65  62 17+
 -8 126 131 12+
  9 208 237 22
  9 229 254  8+
 -9 107 106 13+
 10  45  40 21+
 11  46  77 24+
-11  84 111 17+
   H= 1,K=  2
  0 488 494  9
  0 357 488  4+
  1 294 324  6+
 -1 483 492  3+
  2 459 493 15
  2 442 460  4+
 -2 265 271 52
 -2 254 240  7+
  3 298 317 11
  3 269 293  7+
 -3 413 348 17
 -3 336 337  5+
  4  50  61 23+
 -4 112  79 16+
  5 298 304 47
  5 285 282  7+
 -5 827 706
 -5 620 679  2+
  6 158 187 17
  6 151 161 11+
 -6 203 147  3
 -6 203 174  9+
  7 241 270 30
  7 240 243  8+
 -7 217 219  3
 -7 217 217  9+
 -8 193 191  9+
  9 187 156 15
  9 153 165 11+
 -9 177 123 15
 -9 114 115 12+
 10  84  97 16+
-10 127  89 13
-10 112  94 13+
   H= 1,K=  3
  0 681 924  2+
  1 125 120 16+
 -1 372 357  1
 -1 322 366  5+
  2 184 170  8
  2 211 180  9+
 -2 612 830  2+
  3 190 199 24
  3 198 199 10+
 -3 347 287 10
 -3 301 290  6+
  4 822 783  8
  4 685 756  2+
 -4 682 606 20
 -4 509 583  3+
  5  81  54 17+
 -5 285 277 49
 -5 258 283  8+
  6 113 111 13+
 -7  94  90 14+
  8 149 170 15
  8 139 153 11+
 -8  85  85 15+
  9  77  84 16+
 -9  46  23 20+
 10  56  68 20+
-10 132 126 12+
   H= 1,K=  4
  0 493 561  5
  0 549 552  2+
  1 409 421 34
  1 352 401  5+
 -1 113  83 13
 -1  72  43 22+
  2  40  30 28+
 -2 634 641  5
 -2 569 629  2+
  3 488 514  7
  3 436 495  4+
 -3 151 187  8
 -3 197 197 10+
  4 144 150  8
  4 157 154 12+
 -4 141 132 11
 -4 152 126 12+
  5 478 463  4
  5 422 444  4+
 -5 641 595 21
 -5 514 559  3+
  6 161 192  6
  6 162 176 11+
 -6 159 183  6
 -6 175 169 10+
  7 318 333 11
  7 297 316  6+
 -7  57  66 18+
  8  72  67 16+
 -8  75  69 15+
 -9 149 160 13
 -9 168 159 10+
 10  69  81 18+
-11  57  69 21+
   H= 1,K=  5
  0 167 167 12+
  1 493 483 28
  1 487 464  3+
 -1 156 187 54
 -1 203 178 10+
  2 128 151 27
  2 192 159 10+
 -2  94  97 17+
  3 167 173 41
  3 174 160 11+
 -3 187 189 18
 -3 173 166 11+
  4 552 551 25
  4 485 531  4+
 -4 213 222 32
 -4 204 201  9+
  5 285 308 49
  5 255 282  8+
  6 246 208  1
  6 242 210  8+
 -6 215 195 32
 -6 169 182 10+
  7 108 104 13+
 -7 200 205  9+
  8  63  68 17+
 -8 115 105 12+
  9  87  97 15+
 10  51  19 22+
-10  88 102 15+
-11  80  93 19+
   H= 1,K=  6
  0 121 178 23
  0 166 169 12+
  1 160  83 12+
  2 578 548  1
  2 473 524  4+
 -2 261 258 59

  L  FO  FC WT
 -2 225 234  9+
  3  46  44 23+
 -3 125 100 18
 -3 148 104 12+
  4 179 197 26
  4 130 191 18+
 -5 262 248 53
 -5 258 245  8+
  6 165 160  7
  6 139 124 11+
 -6 149 167 13
 -6 133 132 12+
 -7 133 115 12+
  8  70  71 16+
 -8 165 174 14
 -8 181 178 10+
 10  85 114 17+
-10 129 129 13+
   H= 1,K=  7
  0  96  74 16+
  1 509 531 15
  1 488 507  3+
 -1 234 292 15
 -1 283 285  7+
 -2 157 157 29
 -2 177 166 11+
  3 110 133 14+
 -3  53  44 21+
  4 175 210 16
  4 184 200 10+
 -4 125 112  7
 -4 144 128 12+
  5 149 176  3
  5 127 145 12+
  6  97  81 14+
 -6 139 136 14
 -6 145 133 11+
  7  86  77 14+
 -7 265 260  5
 -7 251 252  7+
 -8  95  77 14+
  9 104 139 14+
-10  46  46 23+
-11  65  84 24+
   H= 1,K=  8
  0 299 345 16
  1 217 219 64
  2 115 142 30
 -2 431 465 16
  3 235 270  6
  4 111 150  4
 -5 144 150 16
   H= 1,K=  9
  0 280 325 12
  1 180 200 32
 -1 135 158 40
  2  86  92 23
 -2 222 233 13
  3 117 141  9
  4 200 241  5
 -4 221 225 31
   H= 1,K= 10
 -1 238 263 22
  3 135 143 17
 -4 139 152  8
  5 177 165 19
 -5 279 280  8
  7 131 106  3
   H= 1,K= 11
 -2 119 126 11
 -3 216 221  5
  4 170 161 13
 -4 223 227 15
   H= 1,K= 12
  2 111  66 14
 -2 196 193 14
   H= 1,K= 14
  2 129  94  9
   H= 2,K=  0
  0 641 801  2+
  2 359 356 39
  2 302 327  6+
 -2 608 528  1
 -2 553 484  2+
  4 473 483 41
  4 460 450  4+
 -4 283 247 16
 -4 232 226  9+
 -6 297 264 11
 -6 255 227  8+
  8 260 252 56
  8 227 247  8+
 -8 200 205 23
 -8 192 186  9+
-10 124 136 11
-10 146 137 11+
-12  64  88 23+
   H= 2,K=  1
  0 228 206 10
  0 238 189  8+
  1 190 206  5
  1 192 208 10+
 -1 746 664 18
 -1 808 605  1+
  2 153 124  7
  2 131 109 15+
 -2 511 440 27
 -2 478 455  3+
  3 338 334 10
  3 272 308  7+
 -3 384 317  2
 -3 386 318  4+
  4  60  15 20+
 -4 678 474  1
 -4 478 467  3+
  5 235 237 63
  5 238 229  8+
 -5 649 539  3
 -5 512 505  3+
  6 285 292 49
  6 272 277  7+
 -6 405 372  7
 -6 366 364  5+
  7 221 215 31
  7 188 183  9+
 -7 125 102 12+
 -8 122 106 12+
  9 112 118  4
  9 120 130 12+
 -9 286 275  7+
 11  89 110 19+
   H= 2,K=  2
  0 7781258  1+
  1 236 242  2
  1 244 279  8+
 -1 558 562 25
 -1 628 554  2+
  2 797 739 17
  2 537 727  3+
 -2 322 280  7
 -2 307 297  6+
  3 281 278 25
  3 258 276  8+
 -3 590 591  2+
 -4 281 253 25
 -4 228 242  9+
  5 484 474 29
  5 411 439  5+
 -5 101  53  4
 -5  86  57 17+
  6  50  39 20+
 -6 218 215 66
 -6 192 194 10+
  7 120 110 19
  7  99 102 14+
 -7 389 387 36
 -7 357 354  5+

  L  FO  FC WT
  9  93 103 14+
 -9  64  73 17+
-10 205 177 13
-10 190 196  9+
 11  54  49 25+
   H= 2,K=  3
  0 426 428 32
  0 456 397  3+
  1  72  58 21+
 -1 804 824 17
 -1 945 817  1+
  2 512 510  3+
 -2 431 440  4+
 -3 233 247  9+
  4 305 311 45
  4 274 288  7+
 -4 557 419  3
 -4 358 402  5+
  5 163 165 28
  5 170 171 11+
 -5  87  50 17+
  6 217 216 64
  6 183 180 10+
 -6 305 298 45
 -6 249 276  8+
 -7  81  70 15+
  8 112 125 13+
 -8  67  75 16+
  9  48  24 20+
 -9  84  80 15+
 10  54  64 21+
   H= 2,K=  4
  1 430 408 32
  1 330 380  6+
 -1 142 131 14
 -1 217 133  9+
  2  35  14 28+
 -2  40  61 28+
  3  88 103 17+
 -3 669 587
 -3 459 564  4+
  4 159 161 88
  4 149 146 12+
 -4 218 197 12
 -4 173 189 11+
  5 477 483 29
  5 393 450  5+
 -5  61  46 19+
  6  53  85 19+
 -6 150 156 31
 -6 126 143 13+
  7  91  94 14+
 -7 297 303 47
 -7 260 267  7+
  8  70  58 16+
 -8  50  12 19+
  9 151 153 30
  9 122 162 13+
 -9 164  23 10+
-10  66  63 17+
-11  51  76 22+
   H= 2,K=  5
  0 327 331 47
  0 350 320  5+
  1 287 308 54
  1 290 308  7+
 -1 492 489 31
 -1 573 469  3+
  2 400 413 35
  2 409 402  4+
 -2  27  12 32+
  3 318 327 44
  3 275 298  7+
 -3 173 163 27
 -3 200 167 10+
  4 349 364 40
  4 302 353  6+
 -4 371 336 37
 -4 287 320  7+
 -5 123 112 28
 -5  74  73 17+
  6 136 132 34
  6 114 111 13+
 -6 132 120 26
 -6 111 107 13+
  7 227 217 61
  7 173 214 10+
 -7 238 227 19
 -7 205 226  9+
  8 141 132 24
  8 122 144 12+
 -9 252 240 55
 -9 236 256  8+
   H= 2,K=  6
  0 714 773
  0 855 761  1+
  1 106 132 16
  1 131 140 13+
 -1 261 256 54
 -1 353 259  5+
  2 449 475 44
  2 437 460  4+
 -2 376 365 39
 -2 319 341  6+
  3  85  88 16+
 -3  89  83 16+
  4 196 195 71
  4 173 158 10+
 -4  54  43 20+
  5 213 226 65
  5 203 223  9+
 -5  58  60 19+
  6 107 115 26
  6  87 100 14+
 -6 200 184 17
 -6 163 154 10+
  7  66  36 16+
 -7  54  48 18+
  8 207 187 67
  8 155 199 11+
 -8  66  36 16+
-10 176 181 10+
   H= 2,K=  7
  0 269 259 52
  0 324 252  6+
  1  48  79 22+
 -1 396 401 39
 -1 509 371  3+
  2 116 138 40
  2 107 131 14+
 -2 210 209 94
 -2 248 204  8+
  3 429 425 46
  3 351 390  5+
 -3  58  49 20+
  4  73  91 16+
 -4  47  50 21+
  5  52  52 19+
 -5 217 215 64
 -5 184 177 10+
 -6  51  47 19+
  7 158 149 44
  7 119 149 12+
 -7 198 209 35
 -7 207 220  9+
  8  58  25 18+
 -8  56  33 18+
  9  64  78 19+
 -9 212 214 22
 -9 209 234  9+
-10  54  47 21+
   H= 2,K=  8
  0 257 272 57
  1 340 350 46
  2 184 190107
 -2  85  81 17
  3  97  68  4

  L  FO  FC WT
 -3 242 244 58
 -4 189 191 74
  5 200 201 69
  6  92 101 19
 -6 170 188 41
 -7 124 108 18
   H= 2,K=  9
  0 166 185 85
  2 178 197 79
 -2 152 149 48
  3  96 113 24
  4 120 121 23
 -4 278 273 50
  5 141 129 24
  6 138 101 20
 -6 164 166 42
   H= 2,K= 10
 -1 126 126 43
 -2  83  78 13
  3 120 110 38
 -3 286 258 12
  5 195 152 35
  6 103  93 22
 -7 205 166 34
   H= 2,K= 11
 -1  90 101 19
 -4 130 101  8
 -5 158 146 17
  6 130  92 21
 -6 133  99  5
   H= 2,K= 12
 -2 101  94 11
  4 145 101 32
  5 128  91 22
   H= 2,K= 14
  0 184 134 10
   H= 3,K=  0
  0 641 636 21
  0 751 594  1+
  2 492 483  9
  2 423 469  4+
 -2 152 159 13
 -2 181 139 11+
  4 303 312 46
  4 264 271  7+
 -4 147 157 15
 -4 111 126 15+
  6 176 191 33
  6 148 165 11+
 -6 242 251 19
 -6 285 272  7+
  8 164 143 31
  8 128 144 12+
 -8 306 329 15
 -8 328 301  6+
 10  64  41 20+
   H= 3,K=  1
  1 444 497  1
  1 447 466  4+
 -1 194 189  9
 -1 208 177 10+
  2  91  76 18+
 -2 177 198  6
 -2 231 180  9+
  3 203 203 23
  3 189 199 10+
 -3 258 224  7
 -3 229 198  9+
  4 413 422  6
  4 360 414  5+
  5 185 235 27
  5 193 193 10+
 -5 209 221  4
 -5 209 206  9+
  6 128 108  7
  6 117  96 13+
 -6 251 243  9
 -6 236 226  8+
  7  57  69 18+
 -7 177 186  8
 -7 167 152 10+
  8  63  89 17+
  9 230 203 30
  9 183 220 10+
 -9 199 175  9+
-10  94  60 14+
-11  89 100 16+
   H= 3,K=  2
  0 507 516 29
  0 531 496  3+
  1 496 455 28
 -1 203 196  9
 -1 249 224  8+
  2 356  40  5+
 -2 256 253 18
 -2 295 245  6+
  3 457 456 43
 -3 627 556 22
 -3 581 550  2+
  4 318 315 11
  4 336 293  6+
 -4 104  79 16+
  5  56  39 19+
 -5 563 510  8
 -5 500 481  3+
  6 116 129 28
  6 110 114 13+
 -6 170 135 27
 -6 170 145 11+
  7 254 233 28
  7 196 223  9+
 -7 141 123 19
 -7 126 104 12+
  8  76 105 16+
 -8 196 203 23
 -8 196 190  9+
  9  64  72 18+
 -9 196 157 17
 -9 172 154 10+
 10  84  96 18+
-10 100  88 14+
-11  90  88 16+
   H= 3,K=  3
  0 451 331  4+
  1 132 156 17
  1 181 154 11+
 -1  44  33 27+
  2 241 266  7
  2 195 240 10+
 -2 561 512  3+
  3 353 344  5
  3 348 350  5+
 -3 294 304  7+
  4 272 343 51
  4 364 320  5+
  5  75  79 16+
 -5  41  55 24+
  6 358 359 39
  6 300 335  6+
 -6 306 309  6+
  7 165 136 21
  7 149 149 11+
 -7  58  38 18+
  8  56  65 18+
 -8 194 179 14
 -8 177 181 10+
  9  81  99 16+
-10 137 122 12+
   H= 3,K=  4
  0 300 315 23
  0 400 307  4+
  1 128 135 13
  1 145 129 13+
 -1 430 421 32
 -1 391 397  5+
  2  39  32 25+
 -2  44  20 25+

  L  FO  FC WT
  3 371 379 12
  3 328 338  6+
 -3 219 212  9+
  4 151 157 15
  4 157 144 11+
  5  42  23 21+
 -5 646 662  2+
 -6  96  75 15+
  7 257 229 54
  7 182 227  9+
 -7  49  36 19+
 -9 108 117 13+
-11  61  71 20+
   H= 3,K=  5
  0 233 227 30
  0 307 218  6+
  1 468 460 15
  1 468 439  4+
 -1  72  62 19+
  2 215 243 16
  2 226 221  9+
 -2 524 485  1
 -2 535 473  3+
  3 384 410 51
  3 389 409  5+
 -3 441 435  4+
  4 180 204 25
  4 177 190 10+
 -4 549 434  3
 -4 362 428  5+
  5 123 165 16
  5 114 132 13+
 -5  56  28 19+
  6  73  82 16+
 -6 287 251 16
 -6 210 229  9+
  7  48  53 19+
 -7 201 147 11
 -7 147 123 11+
  9 112 136 14+
 -9  61  66 17+
   H= 3,K=  6
 01058 923  1+
  1 230 212  8
  1 260 217  8+
 -1  44  50 24+
  2  71  98 18+
 -2 736 706  2+
  3  73  57 17+
 -3 223 217  7
 -3 223 219  9+
  4 245 275 28
  4 217 244  9+
 -4 245 231  8+
  5  54  49 18+
 -5 295 269 15
 -5 237 266  8+
  6  68  80 16+
 -7  70  60 16+
 -8 116 126 12+
-11  48  38 24+
   H= 3,K=  7
  0 173 126 11+
  1 378 378 37
  1 372 345  5+
 -1 129 131 42
 -1 129 118 13+
  2 225 239 62
  2 198 233  9+
 -2 176 190  2
 -2 222 181  9+
  3 121 130 11
  3 124 127 13+
 -3 390 405 35
 -3 386 372  5+
  4  53  47 19+
 -4 142 156 32
 -4 125 155 13+
  5 180 190 38
  5 127 167 12+
 -5 141 117  9
 -5 132 101 12+
 -6 122 115 16
 -6  94 106 14+
 -7 242 173 29
 -7 167 166 10+
  8  81  78 16+
 -8  50  51 19+
  9 101 143 16+
 -9 152 116  3
 -9 123 125 13+
-11  82  86 20+
   H= 3,K=  8
  0 328 319 45
 -1 295 299 67
 -2 105  78 32
  3 158 188 22
 -3 143 105 16
  4 160 150 29
 -5 271 254  1
  6 104  49  4
  7 175 137 20
 -7 138 102 16
 -8 179 102 13
   H= 3,K=  9
  2 118 124 42
 -2 243 243 81
 -3 149 152  3
  4 224 220 62
  6 186 152 25
 -6 229 188 30
   H= 3,K= 10
  3 234 228 60
 -3 174 158 13
 -4 162 138 17
 -5 239 177 29
   H= 3,K= 12
  0 116  87 17
  2 122 100 14
   H= 4,K=  0
  0 376 481 11
  0 603 481  2+
  2 516 535 13
  2 527 505  3+
 -2 527 534 26
 -2 557 507  3+
  4 152 166 11+
 -4  56  47 21+
  6 250 288 28
  6 212 263  9+
 -6 179 192 19
 -6 178 143 10+
 -8 108 107 13+
 10  97 105 18+
-10 269 285  5
-10 316 311  6+
   H= 4,K=  1
  0 210 221 40
  0 249 208  8+
  1 428 459 46
  1 466 448  4+
 -1 664 665 21
 -1 566 648  3+
  2 152 159 18
  2 176 160 11+
  3 114 140  6
  3  86 102 16+
 -3  71  62 20+
  4 365 357  9
  4 319 342  6+
  5 118 131  4
  5 106 114 13+
 -5 202 204  8
 -5 194 170 10+
  6 142 139  7
  6 135 153 11+
 -6 122 103 19

  L  FO  FC WT
 -6 117 103 13+
  7 149 153 11
  7 122 146 12+
 -7 326 345  6
 -7 352 322  5+
  8 111 128 13+
 -8  74  75 16+
 -9 163 168  2
 -9 204 173  9+
-11  77  80 17+
-12  75  85 21+
   H= 4,K=  2
  0 110  86 15+
  1 313 318 63
  1 254 301  5+
 -1 213 199 27
 -1 160 182 12+
  2 340 338 41
  2 309 317  6+
 -2 467 461  5
 -2 458 448  4+
  3 276 267 51
  3 235 247  8+
 -3 195 194 18
 -3 213 175  9+
  4  84  96 16+
 -4 151 155 13
 -4 180 157 11+
  5 305 329  9
  5 253 301  8+
 -5 378 377 18
 -5 377 350  5+
  6  71  62 16+
 -6 277 284 16
 -6 280 260  7+
  7 214 205 32
  7 194 222  9+
 -7 106  89 13+
  8 101  87 14+
  9  65  77 19+
 -9 152 112 13
 -9 131 109 12+
 10  74  74 22+
-10  74  71 16+
   H= 4,K=  3
  0 618 572  5
  0 714 543  2+
  1 175 195 26
  1 266 196  7+
 -1 199 173 35
 -1 181 172 11+
  2 194 194 14
  2 228 188  9+
 -2 194 178  2
 -2 207 183  9+
  3  92  98 15+
  4 426 471  4+
 -4 616 589  2+
  5 138 120 11+
  6  92  48 14+
  7  59   9 18+
 -7  50  40 19+
  8  81  83 16+
 -8  59  54 17+
-10  89  99 15+
   H= 4,K=  4
  0  92  61 17+
  1 199 200 70
  1 258 165  8+
 -1 553 478 25
 -1 427 464  4+
  2 273 266 25
  2 333 251  6+
 -2 202 203 10+
 -3 306 293  2
 -3 310 268  6+
 -4 153  76 12+
  5 290 325  7+
 -5 345 332  6+
 -6  99 103 14+
  7  60  54 17+
 -7 306 309  6+
 -8 104 120 13+
  9 111  92 15+
 -9  62  37 17+
-11  56  33 21+
   H= 4,K=  5
  0 143 126 12+
  1 118 121  9
  1 148 105 12+
 -1 184 205 38
 -1 167 183 11+
  2 126 130 13
  2 135 126 12+
  2 135 126 12+
 -2 169 169  8
 -2 187 178 10+
  3 141 136 12+
 -3 269 260  6
 -3 314 238  6+
  4 214 233  9+
 -4 341 276  6+
  5  63  40 17+
 -5 229 194  8+
  6  58  47 17+
 -6 186 172 10+
  7 140 175 11+
 -7 225 232  8+
  8  94  88 15+
 -8  59  69 17+
 -9 125 119 12+
-11  52  48 23+
   H= 4,K=  6
  0  72  29 18+
  1 147  92 12+
 -1  62  92 19+
  2 291 303 48
  2 308 264  6+
 -2 363 355 38
 -2 312 319  6+
  3  54  68 19+
  4  71  62 16+
 -4 156 139 11+
  5 128 153 12+
 -5  83  69 15+
  6  68  67 16+
 -6 207 179  9+
  7  80  76 16+
 -7  63  68 17+
  8 111 106 14+
-10 172 186 11+
   H= 4,K=  7
  0 127  97 13+
  1 142 149 16
  1 197 132  9+
 -1 189 196 74
 -1 162 171 11+
  2  81  84 16+
  3 100  99 14+
 -3  65  37 18+
 -4 109  79 13+
  5  63  80 17+
 -5 225 182  8+
  6  68  55 16+
 -6  89  93 14+
  7 166 192 11+
 -7 217 181  8+
 -8 103  80 13+
 -9 145 160 11+
   H= 4,K=  8
  0 233 209  8
 -1 128 146 15
  2 255 258 11
 -2 144 165 10
 -3 213 185  2
   H= 4,K=  9
  0 237 241 59

  L  FO  FC WT
 -1 175 191 16
  2 104 112 10
   H= 4,K= 10
  1 184 203 38
   H= 4,K= 12
  2 147 105 15
 -2 115 109 15
   H= 5,K=  0
  0 842 915  1+
  2 372 398 37
  2 503 400  3+
 -2 141 129 13+
  4 372 393 18
  4 388 350  5+
 -4 207 237 22
 -4 240 190  8+
  6 113 108 13+
 -6 355 361 19
 -6 434 346  4+
  8 181 160 10+
 -8 124 111 12+
-10 114 124 11
-10 139 136 12+
   H= 5,K=  1
  0 210 204 74
  0 277 201  7+
  1 308 313 50
  1 413 292  4+
 -1 348 382  6
 -1 345 356  6+
  2 332 346 10
  2 407 328  5+
 -2 342 353 19
 -2 297 338  7+
  3 462 443 10
  3 482 416  4+
 -3 252 278  6
 -3 280 266  7+
  4  47  45 20+
  5 147 133 13
  5 107 115 13+
 -5 228 228  3
 -5 254 188  8+
  6 140  92  3
  6 106  90 13+
 -6 139 175 12
 -6 153 157 11+
  7 106  72 13+
 -7 123 122 16
 -7 171 136 10+
 -8  70  66 16+
  9 124 123 14+
 -9 241 276  1
 -9 319 292  6+
   H= 5,K=  2
  0 260 260 76
  0 290 238  7+
  1 339 356 58
  1 432 326  4+
 -1 206 191 69
  2  86  61 16+
  3 123 116 22
  3 115  94 13+
 -3 422 424 13
 -3 429 394  4+
  4 124  90 12+
  5 185 205 19
  5 188 192  9+
 -5 268 300  8
 -5 341 290  6+
 -6 114 123  4
 -6 143 116 11+
  7 120 109 12+
 -7 220 241 10
 -7 245 213  8+
  8 138 115 12+
 -8 164 147 10+
  9  41  38 27+
-10  68  70 17+
-11  69  88 19+
   H= 5,K=  3
 -1 128 141 18
 -1 159 146 11+
  2 280 277 25
  2 326 232  6+
 -2 424 400 33
 -2 303 358  6+
  3 178 128 10+
 -3 190 195 10+
 -4 178 137 10+
  5  95  67 14+
 -5  50  51 20+
  6 215 195  8+
 -6 384 347  5+
  7  52  32 19+
 -7  52   6 19+
 -8  59  44 17+
 -9  69  19 16+
-10 102  98 14+
   H= 5,K=  4
  0 369 281  5+
  1 142 140 32
  1 302 179  6+
 -1 255 232 27
 -1 274 260  7+
  2 140 131  3
  2 200 130  9+
 -2  93  97 16+
  3 297 313 47
  3 371 296  5+
 -3 406 483  5+
  4 128  94 12+
 -4 145 135 12+
  5 152 117 11+
 -5 346 288  6+
  6 113  94 13+
  7  81  66 16+
 -7 206 152  9+
 -8  94  76 14+
  9  82  84 20+
 -9 124 116 12+
-10  70  79 17+
-11  57  56 22+
   H= 5,K=  5
  1 109  40 14+
 -1 222 223 31
 -1 189 195 10+
  2 104 107 13
  2 113  81 13+
 -2  54  32 20+
  3 129  86 12+
 -3  75  45 17+
  4 219 172  8+
 -4 204 165  9+
  5 133 133 11+
 -5 311 246  6+
  6 156 126 11+
 -6 222 188  8+
  7  88  87 15+
 -7 101  88 13+
 -8  86  89 14+
 -9 145 136 11+
   H= 5,K=  6
  0 399 388 11
  0 407 351  5+
  1  67  35 17+
 -2 126 154  5
 -2 115 144 13+
 -3  80  77 16+
  4 251 197  7+
 -4 163 109 11+
  5  72  29 16+
 -5  74  55 16+
 -6 147 133 11+
 -7  57  51 18+
  8  91  92 17+
 -8 138 101 11+

  L  FO  FC WT
   H= 5,K=  7
  0 115  89 13+
  1 142 146 24
  1 190 129  9+
 -1 350 332 40
 -1 316 305  6+
 -2  45  33 21+
  3 164 132 10+
 -3 130  92 12+
  4 124 128 12+
 -4 168 139 10+
  5  82  74 15+
 -5 159 128 10+
  6  60  44 18+
 -6  89  88 14+
  7  44  36 23+
 -8  54  25 19+
 -9 147 123 12+
   H= 5,K=  8
  0 376 392  1
  2 172 195  7
 -2 154 163  9
 -3 172 191  2
   H= 5,K=  9
  2 180 160 26
 -2 194 203 14
   H= 5,K= 10
 -3 125 117  3
   H= 5,K= 11
 -2 115  88 20
   H= 5,K= 12
  0 152  95 23
   H= 6,K=  0
  0 527 448  3+
  2 156 173 17
  2 222 134  8+
 -2 702 712 20
 -2 631 686  2+
  4 126 143 15
  4 185 135  9+
 -4  70  49 17+
 -6 209 231 22
 -6 251 203  8+
  8  61  49 21+
 -8 131 138 17
 -8 168 132 10+
-10 137 152 12+
   H= 6,K=  1
  0 269 280 54
  0 317 263  6+
  1 409 437 36
  1 469 405  4+
 -1 118 112 16
 -1 151 108 12+
  2 107 112 11
  2 155 104 11+
 -2 196 195  5
 -2 177 187 10+
  3  89  67 15
  3 137  81 11+
 -3 289 300 10
 -3 231 263  8+
 -4 236 278  5
 -4 249 268  8+
 -5 116 106 13
 -5 118 105 13+
  7 109  78 14+
 -7 233 260 15
 -7 303 243  6+
  8  63  52 21+
 -8 150 100  3
 -8 123 103 12+
-10  89  96 15+
-11  67  99 20+
   H= 6,K=  2
  0 141 148 14
  0 176 134 10+
 -1 346 381 40
  2 167 172 83
  2 206 155  9+
 -2 100  90 15+
  3 204 225 20
  3 255 195  7+
  4 132  76 12+
 -4  56  57 19+
  5 135 120 11
  5 183 127  9+
 -5 400 422 35
 -5 449 394  4+
  6  98  74 14+
  7 122  96 13+
 -7 128 102 12+
 -8 106  82 13+
 -9 145 128 11+
-10  85  77 16+
-11  47  46 24+
   H= 6,K=  3
  0 184 212 38
  0 213 174  9+
  1 122  81 13+
 -1  45  52 21+
 -2 377 368 12
 -2 300 347  6+
 -3  58  73 19+
  4 604 411  3+
 -4 196 192  9+
  5 118  95 12+
 -5 150 138 11+
  6 130 109 12+
 -6 212 196  9+
  7  47  23 21+
  8  77  75 19+
 -8  95  86 14+
-10  81  66 16+
   H= 6,K=  4
  0 125 133 10
  0 158 127 11+
  1 147 163 10
  1 206 159  9+
 -1 170 164 27
 -1 152 124 11+
  2 158 172  3
  2 228 158  8+
  3 200 203 23
  3 274 180  7+
 -3 166 195 11+
 -4  68  56 17+
  5 161 120 10+
 -5 375 359  5+
  6 114  86 13+
 -6  73  71 16+
  7 211 196  9+
 -9  59  50 18+
-11  34  46 29+
   H= 6,K=  5
  0 125 145  6
  0 161 125 11+
  1 128 124  9
  1 168  97 10+
 -1  54  51 19+
 -2  80  85 16+
 -3 195 208 12
 -3 164 179 10+
  4 204 166  9+
 -4  89 103 15+
  5 164 129 10+
  6 127 124 12+
 -6 133 129 11+
 -7 102  96 13+
-10  54  68 21+
   H= 6,K=  6
  0  52  48 19+
  2 215 200 13
  2 264 183  7+
 -2 248 249 11
 -2 197 223  9+
  3  79  70 15+

  L  FO  FC WT
 -3  54  23 19+
  4 190 132  9+
 -4  71  44 16+
 -5 123 134 12+
  6  73  83 17+
 -6  69  48 16+
 -8 166 154 10+
-10  55  71 22+
   H= 6,K=  7
  0  56  45 18+
  1 213 217 16
  1 230 200  8+
 -1 132 155 13
 -1 152 154 11+
  2  55  41 18+
 -2  46  53 20+
  3  68  65 16+
 -3  67  43 17+
  5  63  47 18+
  6  55  48 20+
 -6 104  93 13+
 -7 182 158 10+
   H= 6,K=  8
  0 125 124 11
  2 126 125  7
 -2 111 109 21
   H= 6,K=  9
 -2 140 115 25
   H= 6,K= 10
 -1 203 173 13
   H= 6,K= 11
 -2 136 126  6
   H= 6,K= 12
 -2 140 115 25
   H= 7,K=  0
  0 213 246 13
  0 272 223  7+
  2 188 215 24
  2 233 194  8+
 -2 180 240 19
 -2 210 209  9+
  4 167 136  7
  4 225 136  8+
 -6 193 213 36
 -6 186 194  9+
  8  90 107 21+
 -8 102  71 13+
-10  95 116 15+
   H= 7,K=  1
  0  61  58 18+
 -1 306 276 46
 -1 292 245  7+
  2 110 105  4
  2 115  96 13+
 -2  88  55  5
 -2  61  66 18+
  3 155 138  6
  3 157 123 10+
 -3  90  83  5
 -3  78  74 16+
 -4 141 156 19
 -4 130 145 12+
  5  83  69 15+
 -5 206 215 13
 -5 169 187 10+
  6  62  36 18+
 -6 121 108  3
 -6 106 108 13+
  7 113 129 15+
 -7 130 126 15
 -7 124 131 12+
 -9 155 164  3
 -9 153 177 11+
   H= 7,K=  2
  0 244 264 60
  0 303 256  6+
 -1 159 154 34
 -1 193 153  9+
  2 155 159 45
  2 204 152  9+
 -2  89  74 15+
  3 103  72 13
  3 118  80 12+
 -3 317 297 15
 -3 262 270  7+
 -4  50  70 19+
  5 157 134  8
  5 162 140 10+
 -6  99 111 13+
 -7 185 160  4
 -7 151 160 11+
-10  89 120 16+
   H= 7,K=  3
  0 148 150 23
  0 177 120 10+
 -1  59  52 18+
  2 165 148  2
  2 187 134  9+
 -2 165 168 17
 -2 158 147 11+
  3 164 115 10+
 -3 118 141 13+
  4 140 115 11+
 -4 191 256  9+
 -5  47  56 20+
  6 103  94 15+
 -6 108 130 13+
  7  34   7 29+
 -7 128 135 12+
 -8  56  40 18+
-10  40  25 25+
   H= 7,K=  4
  1 184 202 25
  1 218 179  8+
 -1  48  33 20+
  2  62  63 17+
 -2 198 192 17
 -2 177 182 10+
  3  59  35 17+
 -3 227 213  8
 -3 187 184  9+
  4  60  41 18+
 -4  64  76 17+
  5 167 161 10+
 -5  57   9 18+
 -6  68  84 16+
  7  32  32 30+
 -7 127 126 12+
 -8  59  47 18+
 -9  60  80 19+
   H= 7,K=  5
  0 108 104 13+
  1  75  81 15+
 -1 241 232 58
 -1 212 213  9+
  2 136 127 34
  2 145 129 11+
 -3  60  63 17+
  4 189 173  9+
 -4  44  32 20+
 -5 102 133 13+
  6  39   8 25+
 -7 113 136 13+
 -9  77  94 17+
   H= 7,K=  6
  0 206 192 13
  0 217 190  8+
  1  77  48 15+
 -1 108 126 13+
  2 323 286  7
  2 322 302  6+
 -2  61  66 17+
  4  79  85 16+
  6  50  61 23+
 -6 139 157 11+
-10  68 111 21+
   H= 7,K=  7

  L  FO  FC WT
  0  95  79 14+
  1  99  93 14
  1  98 102 14+
 -1 265 241 26
 -1 250 239  7+
  2  89  78 14+
 -2  61  77 17+
  3 132 128 12+
 -3  44  44 20+
  4 109 116 14+
 -5  97 116 14+
 -6  47  32 20+
 -7  63  74 18+
 -8  55  73 20+
 -9  72 121 19+
   H= 7,K=  8
  1 151 144 15
 -2 158 157 17
   H= 7,K=  9
  0 125 113  3
   H= 7,K= 10
 -3 200 127  3
   H= 8,K=  0
  0 146 116  3
  0 129  91 12+
  2 111  84 14
  2 141  85 11+
 -2  67  51 16+
  4 177 160 13
  4 174 169 10+
 -4 173 178 26
 -4 145 157 11+
  6  45  52 24+
 -6 107 109 11
 -6  79 122 15+
 -8 127 129 18
 -8  91 133 15+
   H= 8,K=  1
  1 147 114 13
  1 137 100 11+
 -1  88  72 14+
  2  72  61 16+
 -2 117 104  8
 -2 106  92 13+
  3  86  73 15+
 -3 145 123  3
 -3 122 104 12+
  4 142 112 12+
 -4  64  76 17+
  5  94  90 15+
 -5 128 125 15
 -5 108 121 13+
  6  86 100 18+
 -6 158 149  2
 -6 119 155 12+
 -7 128  82  3
 -7  62  81 17+
 -9  51  72 21+
   H= 8,K=  2
  0 262 273 25
  0 305 277  6+
  1  56  43 18+
  2  68  54 16+
 -2 126 116 18
 -2 144 119 11+
  3 154 138 15
  3 156 144 11+
 -3 193 192 15
 -3 190 188  9+
  4  93  76 15+
 -4  49  58 19+
 -5 207 218 67
 -5 185 222  9+
 -7  54  80 18+
 -8  64  98 18+
   H= 8,K=  3
  0  43  38 20+
  1  81  71 15+
 -1  97  99 14+
  2 194 188  2
  2 189 193  9+
 -2 226 199 30
 -2 188 181  9+
  3  95  83 14+
 -3  62  59 17+
  4  77  70 16+
 -4  58  64 18+
  5  58  56 20+
 -5  44  33 20+
  6  78  79 19+
 -6 144 155 11+
 -7  43  33 21+
 -8  39  25 22+
-10  48  71 24+
   H= 8,K=  4
  1 121 113 12+
 -1 222 209 15
 -1 219 207  8+
  3  93 108 14+
 -3 167 151  5
 -3 150 151 11+
  4  73  57 17+
 -5 179 213 10+
 -9  48  66 22+
   H= 8,K=  5
  0  55  52 18+
  1 180 169 39
  1 188 175  9+
  2  89  75 15+
 -2 248 232 56
 -2 203 241  9+
  3 119 121 13+
 -3  90  79 14+
  4  59  61 19+
 -6  84 100 15+
 -9  53  92 22+
   H= 8,K=  6
  0 269 241 26
  0 256 254  7+
 -1  42  13 20+
 -2 115  92 20
 -2 101  98 13+
 -3  67  81 16+
  4  83  77 17+
 -4  82  78 15+
 -5  96 116 14+
 -8  71  96 18+
   H= 8,K=  7
  1 151 114 10
  1 130 119 12+
 -1  83  86 15+
  2  78  86 16+
 -2 112 110 13+
  3  67  43 18+
 -3 124 122 12+
  5  34  35 31+
 -7  38  34 24+
 -9  52  74 25+
   H= 8,K=  9
 -2 162 115  2
   H= 9,K=  0
  2 229 204 30
  2 245 219  8+
 -2 113  87 11
 -2  61  76 17+
 -6  98  74 13
 -6  70  68 16+
 -8 101 113 15+
-10  86 108 20+
-12  77  76 20+
-12  65 105 24+
   H= 9,K=  1
  1 153 116  5
  1 133 120 12+
 -1 145 136 29
 -1 155 141 11+
  3  59  60 19+

  L  FO  FC WT
 -3  59  40 17+
  4  87  83 17+
 -5  50  39 19+
 -7 135 120  3
 -7 106 129 14+
 -8  42  45 23+
 -9  42  34 25+
-10  29  53 35+
   H= 9,K=  2
  0  72  65 16+
  1 105  83 13+
 -1  70  55 16+
  2  99  94 14+
 -2 147 128 13
 -2 156 131 10+
  3  90  86 15+
  5  58  77 23+
 -5 100  96 14+
 -6  48  36 20+
 -9  52  73 23+
-10  34  60 34+
   H= 9,K=  3
  0 121 122 11
  0 131 122 12+
 -1  48  43 19+
  2  44  31 21+
 -2  85  84 15+
 -3  67  56 16+
  4 127 143 14+
 -4 129 136 12+
  5  39  39 29+
 -5  40  50 21+
 -6  46  62 20+
   H= 9,K=  4
 -1 175 160  8
 -1 162 170 10+
  2  89  82 15+
 -2  63  71 17+
 -3  89  82 14+
 -4  58  55 18+
  5  59  56 25+
 -5 136 159 12+
 -7  63  85 18+
   H= 9,K=  5
  1 113 113 13+
 -1  88  92 15+
 -2  56  75 18+
 -3 105 136 13+
 -4 119 142 13+
 -5  73  81 16+
 -6  45  45 21+
 -7  52  68 21+
   H= 9,K=  6
 -2 230 196 30
 -2 174 212 10+
 -6  79 100 17+
   H= 9,K=  7
  0  48  59 21+
  1  48  51 22+
 -1 105 101 14+
 -3  65  70 18+
 -4  57  61 19+
 -5  48  66 21+
 -7  60  86 21+
   H=10,K=  0
  0 241 205 30
  0 252 225  8+
  2 124 113 14+
  4  66  69 24+
 -6 102 112 14+
 -8  53  44 23+
   H=10,K=  1
 -1 192 143 36
 -1 160 155 11+
  2  90  84 16+
 -2 102 107 14+
  3  85  85 18+
  4  33  51 34+
 -4  63  19 18+
 -5  87  80 15+
 -9  59  83 25+
   H=10,K=  2
  1 127 119 13+
 -1  61  57 18+
 -3 123 121 13+
 -4  47  58 20+
 -5  42  42 22+
 -6  51  58 21+
 -7  45  52 23+
 -8  46  63 25+
   H=10,K=  3
  0  44  33 22+
  1  38  41 24+
  2  60  70 21+
 -2  90 100 15+
  3  25  16 34+
 -4  59  54 19+
 -6 108 133 14+
   H=10,K=  4
  0  49  54 21+
  2  53  12 22+
 -3 127 142 13+
 -5  76  87 17+
 -7  52  72 22+
   H=10,K=  5
  2  37  37 28+
 -5  68  86 18+
 -6  48  60 23+
   H=10,K=  6
 -4  41  37 24+
 -6  51  70 23+
 -7  29   3 33+
   H=10,K=  7
 -1  49  47 23+
 -5  43  41 25+
   H=11,K=  0
  0  74  66 19+
 -2 132 124 13+
 -4  35  33 26+
 -6  36  37 28+
   H=11,K=  1
  0  35  38 27+
  1  76  82 20+
 -1  37  35 26+
 -2  62  57 20+
 -3  85  84 17+
 -4  66  67 19+
 -6  35  46 28+
 -7  39  53 29+
   H=11,K=  2
 -1 113 100 15+
  2  27  37 40+
 -5 106 118 15+
   H=11,K=  3
  1  23  11 38+
 -2  84  90 17+
 -3  43  63 24+
 -4  42  44 25+
 -6  43  55 27+
   H=11,K=  4
 -2  41  50 25+
 -3  51  67 23+
 -5  64  74 21+
   H=11,K=  5
 -6  20  37 44+
   H=12,K=  0
 -2  70  72 24+
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[a] Values of $F_o$ and $F_c$ are multiplied by a factor of 7. $WT = \sqrt{w}$. Precession data are denoted by a + symbol.

made for these atoms from the crystal structure of iodopentamethylenetetrazolium chloride investigated by Baenziger and Nelson and independently determined by Tulinsky, Bloor, and Popov.[4] The organic moiety of this compound consists of a tetrazole ring to which a five-membered chain is attached through the carbon atom at position 5 and the nitrogen at position 1. The iodine coordinates to the nitrogen at position 4. In both structures, the site of coordination is N(4) with the carbon atom immediately adjacent.

Since hydrogen atom positions were not apparent from difference maps, hydrogen atoms were placed at fixed positions next to the methyl carbon atoms and the atoms chosen as the carbon atoms in the ring (to give reasonable bond distances and angles) and given a fixed isotropic temperature factor. [The rationale for this step is that a model including hydrogen atoms most likely near the correct positions would be better suited for locating the carbon atom positions than a model which ignored the contribution of the hydrogen atoms and which would cause the carbon atoms to seek positions to compensate for the H atom omission.] At the end of the refinement with anisotropic temperature factors for all nonhydrogen atoms, $R_H = 0.097$ and the average parameter shifts were less than half the estimated standard deviation.

## Results and Discussion

The final atomic parameters are listed in Table I. The calculated and observed structure factors are given in Table II. Figure 1 illustrates the spatial features of the molecular unit projected onto the (010) plane. Table III lists bond lengths and angles for the molecular unit. The ligands coordinated to zinc appear at the apexes of a distorted tetrahedron. The undistorted tetrahedral angle of 109.5° has increased to 118.4 (2)° in the Cl–Zn–Cl bond angle while the N–Zn–N bond angle has decreased to 98.9 (3)°. The remaining angles about Zn remain roughly tetrahedral. Specifically, they are 111, 109, 108, and 109° (esd ~0.4°). The bond angles and distances about the zinc atom in ZCTZ appear near the extremes of the values determined for other structures as shown in Table IV; the Zn–Cl bond appears to be shortened while the Zn–N bond appears to be lengthened. The Zn–Cl and Zn–N bond distances determined for ZCTZ agree within experimental error with corresponding distances determined for the zinc dichloride complexes of 2,9-dimethyl-1,10-phenanthroline (DMPZC) determined by Preston[5] and 1,10-phenanthroline (PZC) determined by Reimann[14] (Table

TABLE III

BOND LENGTHS AND ANGLES[a]

Distances, Å

| | | | |
|---|---|---|---|
| Zn–Cl(1) | 2.206 (5) | C(5)–N(1) | 1.28 (2) |
| Zn–Cl(2) | 2.198 (5) | N(1)–C(6) | 1.45 (3) |
| Zn–N(4) | 2.04 (1) | N′(1)–N′(2) | 1.32 (2) |
| Zn–N′(4) | 2.06 (1) | N′(2)–N′(3) | 1.27 (2) |
| N(1)–N(2) | 1.36 (2) | N′(3)–N′(4) | 1.31 (2) |
| N(2)–N(3) | 1.31 (2) | N′(4)–C′(5) | 1.30 (2) |
| N(3)–N(4) | 1.36 (2) | C′(5)–N′(1) | 1.32 (2) |
| N(4)–C(5) | 1.30 (2) | N′(1)–C′(6) | 1.49 (2) |

Bond Angles, deg

| | | | |
|---|---|---|---|
| Cl(1)–Zn–Cl(2) | 118.4 (2) | Zn–N(4)–C(5) | 133 (2) |
| Cl(1)–Zn–N(4) | 111.0 (4) | Zn–N(4)–N(3) | 121 (2) |
| Cl(1)–Zn–N′(4) | 109.5 (4) | N(4)–C(5)–N(1) | 110 (2) |
| Cl(2)–Zn–N(4) | 107.8 (4) | C′(5)–N′(1)–C′(6) | 127 (2) |
| Cl(2)–Zn–N′(4) | 109.4 (4) | N′(2)–N′(1)–C′(6) | 125 (2) |
| N(4)–Zn–N′(4) | 98.9 (3) | C′(5)–N(1)–N′(2) | 107 (1) |
| C(5)–N(1)–C(6) | 133 (3) | N′(1)–N′(2)–N′(3) | 107 (2) |
| N(2)–N(1)–C(6) | 117 (2) | N′(2)–N′(3)–N′(4) | 111 (1) |
| C(5)–N(1)–N(2) | 110 (2) | N′(3)–N′(4)–C′(5) | 107 (1) |
| N(1)–N(2)–N(3) | 104 (2) | Zn–N′(4)–C′(5) | 132 (2) |
| N(2)–N(3)–N(4) | 110 (2) | Zn–N′(4)–N′(3) | 121 (1) |
| N(3)–N(4)–C(5) | 105 (1) | N′(4)–C′(5)–N′(1) | 108 (2) |

[a] The estimated standard deviation in the last digit is given in parentheses.

TABLE IV

COMPARISON OF BOND DISTANCES (Å) AND ANGLES (DEG) FOR SOME ZINC COMPLEXES

| Zn–Cl | Cl–Zn–Cl | Zn–N | N–Zn–N | Compound | Coordin about zinc | Ref |
|---|---|---|---|---|---|---|
| 2.198<br>2.206 | 118.4 | 2.04<br>2.07 | 98.9 | This study | Tet | |
| 2.20 | 121.2 | 2.07<br>2.08 | 82.3 | Dichloro(2,9-dimethyl-1,10-phenanthroline)zinc(II) | Tet | *c* |
| 2.207<br>2.198 | 114.7 | 2.050<br>2.072 | 80.4 | Dichloro(1,10-phenanthroline)zinc(II) | Tet | *d* |
| 2.258 | 111.5 | 1.995 | 105.2 | Bis(imidazole)zinc(II) dichloride | Tet | *e* |
| 2.18 | | 2.00<br>2.02 | | Bis(pyridine)zinc dichloride | Tet | |
| 2.24 | 106.3<br>110.7 | 2.09 | 89.1[a] | Monothiosemicarbazide–zinc chloride | Tet | *g* |
| 2.25 | 109.5 | | | $(NH_4)_3ZnCl_5$ | Tet | *h* |
| 2.26 | | | | $Na_2ZnCl_4 \cdot 3H_2O$ | Tet | *i* |
| 2.27<br>2.29<br>2.30 | 108.3<br>112.8 | | | $((CH_3)_4N)_2ZnCl_4$ | Tet | |
| 2.30 | | 2.01 | | $Zn(NH_3)_2Cl_2$ | Tet | *k* |
| 2.55 | | | | Sum of ionic radii | | *l* |
| | | 2.04 | | Bis(L-histidino)zinc(II) dihydrate | Tet | *m* |
| | | 2.00<br>2.05 | | Bis(histidino)zinc(II) pentahydrate | Tet | *n* |
| | | 2.099 | 81.5[b] | Zinc 8-hydroxyquinolinate dihydrate | Tet | *o* |
| | | 1.99 | | Bis(imidazolo)zinc | | *p* |
| 2.58 | | 2.15 | | Bis(hydrazine)zinc(II) dichloride | Oct | *q* |
| | | 2.179<br>2.206 | | *catena*-Di-μ-hydrazine-zinc diacetate | Oct | *r* |
| 2.25<br>2.27 | 112.0 | | | Terpyridylzinc(II) chloride | Trigonal bipyramid | *s* |

[a] N–Zn–S bond angle. [b] N–Zn–O bond angle. [c] H. S. Preston and C. H. L. Kennard, *Chem. Commun.*, 708 (1967). [d] C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966). [e] B. K. S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1966). [f] Yu. A. Sokolova, L. O. Atovmyan, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **7**, 855 (1966); *Chem. Abstr.*, **66**, 49971 (1967). [g] L. Cavalca, M. Nardelli, and G. Branchi, *Acta Crystallogr.*, **13**, 688 (1960). [h] H. P. Klug and L. Alexander, *J. Amer. Chem. Soc.*, **66**, 1056 (1944). [i] B. Brehler, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **114**, 66 (1960). [j] J. R. Wiesner, R. C. Strivatava, C. H. L. Kennard, M. DiVaira, and E. C. Lingafelter, *Acta Crystallogr.*, **23**, 565 (1967). [k] C. H. Macgillavry and J. M. Bijovet, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem., Abt. A*, **94**, 249 (1936). [l] L. Pauling, *J. Amer. Chem. Soc.*, **49**, 765 (1927). [m] R. H. Kretsinger, F. A. Cotton, and R. F. Bryan, *Acta Crystallogr.*, **16**, 651 (1963). [n] M. M. Harding and S. J. Cole, *ibid.*, **16**, 643 (1963). [o] G. J. Palenik, *ibid.*, **17**, 696 (1964). [p] B. Strandberg, B. Svensson, and C. I. Branden, to be submitted for publication (see ref *e*). [q] A. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Crystallogr.*, **16**, 498 (1963). [r] A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfridi, *ibid.*, **19**, 548 (1965). [s] F. W. B. Einstein and B. R. Penfold, *ibid.*, **20**, 924 (1966).

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(14) C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).

TABLE V

OUT-OF-PLANE DISPLACEMENTS[a]

$$-0.61388X - 0.77351Y - 0.15955Z + 1.95177 = 0$$

| | | | |
|---|---|---|---|
| N(1) | −0.015 | N(4) | −0.020 |
| N(2) | 0.018 | C(5) | 0.028 |
| N(3) | −0.003 | C(6) | −0.008 |
| | | Zn | −0.006 |

$$0.52778X - 0.77588Y - 0.34563Z + 1.45048 = 0$$

| | | | |
|---|---|---|---|
| N′(1) | −0.008 | N′(4) | −0.030 |
| N′(2) | −0.036 | C′(5) | 0.010 |
| N′(3) | 0.050 | C′(6) | 0.014 |
| | | Zn | −0.131 |

[a] The equations of the least-squares planes are referred to *a*, *b*, and *c**. Zn was not included in the calculation of the plane.

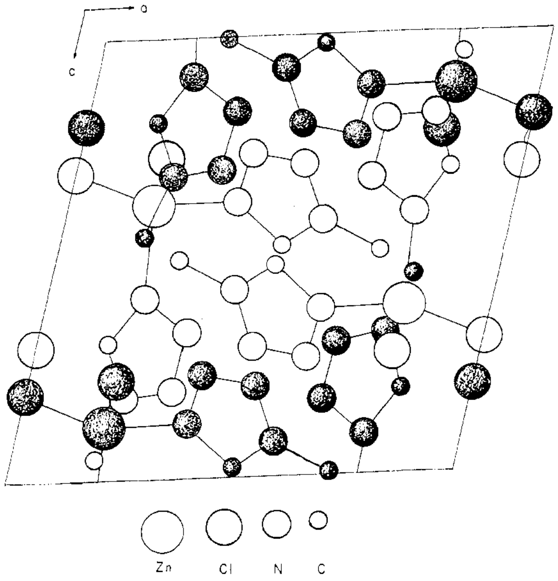

Figure 2.—Structure of ZCTZ projected on (010) showing packing of the molecules.

TABLE VI

COMPARISON OF BOND DISTANCES (Å) IN VARIOUS TETRAZOLE DERIVATIVES

| | This work[a] | 5-Aminotetrazole monohydrate[c] | Hydrazine salt of 5-aminotetrazole[d] | Sodium tetrazolate monohydrate[e] | 2-Methyl-5-aminotetrazole[f] | 1,3-Dimethyl-5-iminotetrazole[g] | Pentamethylene-tetrazole[h] |
|---|---|---|---|---|---|---|---|
| N(1)–N(2) | 1.34 | 1.381 | 1.346 | 1.348 | 1.34 | 1.35 | 1.38 |
| N(2)–N(3) | 1.29 | 1.255 | 1.295 | 1.310 | 1.29 | 1.30 | 1.28 |
| N(3)–N(4) | 1.33 | 1.373 | 1.356 | 1.348 | 1.32 | 1.31 | 1.39 |
| N(4)–C(5) | 1.30 | 1.321 | 1.318 | 1.329 | 1.35 | 1.36 | 1.33 |
| C(5)–N(1) | 1.30 | 1.329 | 1.302 | 1.329 | 1.32 | 1.38 | 1.34 |
| $T^2$ test[b] | . . . | D | S | S | S | D | D |

[a] Estimated standard deviations are 0.02 Å. [b] Results of a $T^2$ test which compares the bond distances of this study to the results for other tetrazole derivatives. S indicates that the differences in the two structures are the result of random fluctuations, tested at the 95% level of significance. (Identical results are obtained at the 99% level.) D indicates that fluctuations in the bond distances of the two structures are due to some systematic effect rather than random fluctuations; the significance is tested at the 99% level. [c] K. Britts and I. L. Karle, *Acta Crystallogr.*, **22**, 308 (1967). [d] J. H. Bryden, *ibid.*, 11, 31 (1958). [e] G. J. Palenik, *ibid.*, **16**, 596 (1963). [f] J. H. Bryden, *ibid.*, **9**, 874 (1956). [g] J. H. Bryden, *ibid.*, **8**, 211 (1955). [h] Reference 4.

IV). At the same time these latter structures show changes in the tetrahedral geometry about the zinc atom of about the same magnitude and in the same direction as found for ZCTZ. The small N–Zn–N angles in DMPZC and PZC result from the fact that the coordination sites on phenanthroline are rigidly held and cannot move apart in response to changes in the orbital geometry about the zinc atom.

The expansion of the Cl–Zn–Cl bond angle would increase the s character of the Zn orbitals to Cl thereby causing a shortening of the Zn–Cl bond. The corresponding increase in p character for the Zn orbitals to N would be expected to result in an increased Zn–N bond length.[15] The decreased N–Zn–N angle may be due to restrictions caused by the packing in the cell. As seen from Figure 2, the tetrazole ligands lie within a band parallel to the (100) plane in the central region of the cell. The N–Zn–N bond angle of 98.9 (3)° may be thought to result from the competing factors of cell packing which would tend to decrease the angle in the case of ZCTZ and the tendency of Zn to achieve tetrahedral symmetry which would result in an angle of 109.5°. The apparently less crowded volume along the *yz* plane, which contains the Cl(1) atoms, may explain the ability of Zn to allow an unexpectedly large Cl–Zn–Cl angle of 118°.

The tetrazole rings are planar (Table V) within the experimental uncertainties in the positions of the atoms. The zinc atom is planar with the tetrazole ring, N(1)–C(6), within experimental error. However, the zinc atom is significantly out of the plane of the other tetrazole ring. The Zn–N′(4) vector makes an angle of 3.6° with the plane of the ring. This lack of planarity would somewhat reduce the overlap of the N′(4) orbital with Zn as shown by a slightly lengthened Zn–N′(4) bond.

Comparable distances in the two tetrazole rings do not agree identically. By application of a $T^2$ test,[16] however, it is found that the differences in the corresponding distances in the rings are not significantly different from the averaged distances at the 10% level of significance. The interatomic distances found for the 1-methyltetrazole ring are tabulated in Table VI along with the corresponding distances for some other tetrazole derivatives. All ring distances of 1-MeTz agree within experimental error with the distances for 5-

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(15) R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966, p 146.

(16) "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959, p 94.

aminotetrazole (Britts and Karle[17]), the hydrazine salt of 5-aminotetrazole (Bryden[18]), and sodium tetrazolate monohydrate (Palenik[19]).

The nature of the Zn–Tz interaction may be summarized by comparing the results of this study with the results of the determination of the crystal structure of the iodopentamethylenetetrazolium monochloride complex (PMTICl) by Baenziger and Nelson.[4]

In both complexes the following statements apply. The moiety coordinated to the tetrazole ring is essentially planar with the ring. The site of coordination to the tetrazole ring is identical (labeled N(4) in ZCTZ, N(2) in PMTICl). The coordination geometry at N(4) is essentially identical. Denoting values for the corresponding angles of PMTICl by an asterisk, the bond angles (degrees) about N(4) are as follows: N(3)–N(4)–C(5), 105 (2), 107 (2), 106* (4); N(3)–N(4)–Zn, 121 (2), 121 (2), 125* (4); C(5)–N(4)–Zn, 132 (2), 133 (2), 130* (4). These considerations suggest that the preferred mode of coordination in ZCTZ (and PMTICl) is by means of a charge-transfer σ bond to position N(4) of the tetrazole ring.

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[17] K. Britts and I. L. Karle, *Acta Crystallogr.*, **22**, 308 (1967).

[18] J. H. Bryden, *ibid.*, **11**, 31 (1958).

[19] G. J. Palenik, *ibid.*, **16**, 596 (1963).

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Contribution from the Department of Chemistry
and the Polymer Research Institute of the Polytechnic Institute of Brooklyn, Brooklyn, New York

# Optically Active Boron. The Crystal Structure of (+)-4-Methylpyridinetrimethylaminebromohydroboron Hexafluorophosphate

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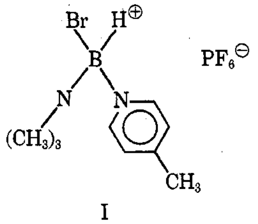
The first crystal structure of a stable optically active compound having a boron atom as the asymmetric center has been elucidated. (+)-4-Methylpyridinetrimethylaminebromohydroboron hexafluorophosphate (I) crystallizes in the monoclinic system, space group $P2_1$, with $a$ = 19.35 (1) Å, $b$ = 7.870 (4) Å, $c$ = 10.549 (5) Å, $\beta$ = 90° 25′ (10′). Two crystallographically independent formula units are present in the unit cell. The structure has been solved by Patterson and Fourier methods and refined to an $R$ factor of 0.089 for 2481 independent nonzero reflections measured with counter technique (Cu Kα); the disagreement factor increases to 0.102 if 481 reflections below the limit of detectability are included. The geometrical parameters of the two independent cations, as well as of the two independent anions, are virtually identical. An almost regular sp$^3$ hybridization of the boron atom results from the arrangement of the surrounding ligands. The stereochemistry of the cations is discussed on the basis of intra- and intermolecular interactions; the presence of two pairs of independent ionic species is rationalized in terms of the tendency to produce a pseudocentrosymmetric packing.

## Introduction

Recently Ryschkewitsch and Garrett have reported the preparation and the resolution of the first examples of stable optically active compounds with the boron atom as the asymmetric center.[1] While the isoelectronic and isosteric analogs of this compound, having optically active carbon or nitrogen atoms, have never been resolved, the boron salts have proven to be highly stable toward racemization during the fractionation process. In view of the interest involved in the stereochemical knowledge of such compounds, we have undertaken a single-crystal X-ray investigation of one of them, namely, (+)-4-methylpyridinetrimethylaminebromohydroboron hexafluorophosphate (I). We now report the results of the detailed analysis of the crystal and molecular structure of I.



I

## Experimental Section

Colorless, needlelike single crystals of I, obtained from an acetone–water mixture (mp 136–137°, $[\alpha]_D$ −60.9°), were kindly donated by Dr. Ryschkewitsch. A small crystal of approximately cylindrical shape ($r \simeq 0.05$ mm, length $\simeq$0.5 mm) was used for the X-ray investigation. From preliminary Weissenberg photographs the crystal was found to belong to monoclinic space group $P2_1$ (systematic ($0k0$) absences with $k$ odd). A Picker four-circle automated diffractometer equipped with a PDP-8 digital computer was used for the collection of the intensity data. The unit cell dimensions were obtained from a least-squares treatment of the $2\theta$, $\chi$, and $\varphi$ setting angles of 12 reflections with $2\theta >$ 80°, using a program prepared by Busing and Levy.[2] The resulting parameters are $a$ = 19.35 ± 0.01 Å, $b$ = 7.870 ± 0.004 Å, $c$ = 10.549 ± 0.005 Å, $\beta$ = 90° 25′ ± 10′, $d_{\text{X-ray}}$ = 1.607 (1) g/cm$^3$ with $Z$ = 4, $d_{\text{exptl}}$ = 1.58 (2) g/cm$^3$ (flotation), $\mu$ = 51.56 cm$^{-1}$, and $\lambda_{\text{Cu}K\alpha}$ 1.5418 Å.

The experimental density agreed reasonably with the calculated density assuming four molecules of I per unit cell, thus requiring the presence of two crystallographically independent formula units. A total of 2962 integrated intensities were collected using a $\theta$–$2\theta$ scan mode (1.67°) with Ni-filtered Cu Kα radiation in the range 0–130° of $2\theta$. Two stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of each scan. Since $\mu$ = 51.66 cm$^{-1}$ (λ 1.5418 Å) and

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[1] G. E. Ryschkewitsch and J. M. Garrett, *J. Amer. Chem. Soc.*, **90**, 7234 (1968).

[2] Z. W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).