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The crystal and molecular structure of trans-diiodotetra(ethylenimine)rhodium(III) iodide. trans-[Rh- $(Az)_{4}I_{2}$ ]I, has been determined by single-crystal X-ray diffraction methods. The multiple film equiinclination Weissenberg method was used to collect 890 non-zero reflections. The complex crystallizes in the tetragonal space group  $P\overline{4}n2$  with a cell of dimensions a =7.81(1) Å, c=14.26(2) Å and V=869.3 Å<sup>3</sup>. The experimental density of  $2.48 \pm .04$  g/cm<sup>3</sup> is consistent with a calculated value of 2.51 g/cm<sup>3</sup> for two molecules in the unit cell (Z=2). Positional, scale and thermal parameters have been refined by least squares methods to a conventional R factor of .075. The  $[Rh(Az_4I_2]^+$  unit is crystallographically required to possess  $D_2$  symmetry with Rh in the 2(d) special positions of the space group. The coordination geometry about Rh is essentially a tetragonally distorted octa-The ethylenimine nitrogen atoms alternate hedron. slightly above and below the equatorial plane of the distorted octahedron.

## introduction

This work was undertaken in order to determine the structure of the complex  $[Rh(Az)_3I]$  which had been reported earlier.<sup>1</sup> The symbol Az will be used for ethylenimine which is also called aziridine. The complex  $[Rh(Az)_3I]$  is unusual since the Rh atom is apparently in its unipositive state and there are no strong  $\pi$ -bonding ligands present which are usually required to stabilize the +1 oxidation state of Rh.

An attempted synthesis of the  $[Rh(Az)_3I]$  complex following the procedure first reported by Scherzer *et. al.*,<sup>1</sup> led to the isolation of a brown material which after several recrystallizations gave several small brown crystals. Since insufficient material was available for an elemental analysis, it was assumed these crystals were of the proper complex. The crystals turned out to be of the Rh<sup>III</sup> complex *trans*-[Rh(Az)<sub>4</sub>-I<sub>2</sub>]I and the crystal and molecular structure of this compound is reported here. The structure apears to be of particular interest since it represents the first *reported* structure of a complex containing aziridine as a coordinated ligand.

(1) J. Scherzer, P. K. Phillips, L. B. Clapp, and J. O. Edwards, Inorg. Chem., 5, 847 (1966).

## **Experimental Section**

Crystal Preparation. The complex  $[Rh(Az)_4I_2]I$  was prepared from the analogous chloride complex by the method of Scherzer *et al.*<sup>1</sup> 3 g of  $[Rh(Az)_4CI_2]CI$  were dissolved in 40 ml of distilled water and 1.2 g of silver oxide were added. The mixture was heated on a steam bath for 45 minutes. After filtering this solution, 3.0 g of KI were added and heating was continued for 15 minutes. The dark brown precipitate that formed upon heating, was suction filtered and then recrystallized from methanol. The crystal used in the X-ray work was grown by seeding a saturated methanol solution with a few very small crystals.

Unit Cell and Space Group Determination. The crystals were examined by optical goniometry and Weissenberg and precession photography. On the basis of these examinations, the crystals were found to belong to the tetragonal system with a unit cell of dimensions a = 7.81(1) Å, c = 14.26(2) Å and V = 869.3Å<sup>3</sup>. The unit cell dimensions were measured from precession photographs taken with  $MoK_{\alpha}$  radiation. No correction was made for possible film shrinkage. The observed extinctions, O k 1 for k+1 odd, are consistent with the two acentric space groups P4n2  $(D_{2d}^8)$  and P4<sub>2</sub>nm $(C_{4v}^4)$ . In addition, it was also observed that the reflections for which the sum h+k+1is even, were generally more intense than those for which h+k+1 is odd.

An experimental density of  $2.48 \pm 0.04$  g/cm<sup>3</sup> obtained by flotation in methylene chloride-methylene iodide solutions was not consistent with a calculated density 2.74 g/cm<sup>3</sup> for four molecules of  $[Rh(Az)_3I]$  per unit cell. The observed density was, however, close to the value of 2.51 g/cm<sup>3</sup> calculated for two molecules of the closely related Rh<sup>III</sup> complex [Rh-(Az)\_4I\_2]I per unit cell. The crystal morphology was C<sub>4v</sub> with the { 101} faces showing development. The volume of the crystal used for the collection of intensity data was calculated to be  $6.0 \times 10^{-3}$  mm<sup>3</sup>.

Collection and Reduction of the Intensity Data. Intensity data were collected at room temperature by the equiinclination Weissenberg technique using Zr-filtered Mo K<sub>a</sub> ( $\lambda$ =0.7107 Å) radiation. The crystal was mounted along the *c* axis and the layers h k 0 to h k 16 were recorded on multiple films. The intensities of 890 reflections accessible within the angular range  $\Theta_{Mo} \leq 23.5^{\circ}$  were estimated visually using a caliTable I. Observed and Calculated Structure Factor Amplitudes (in electrons × 10) for [Rh(Az),I2]I

| H. R. FORS FORL  | H & F. M. FCH  | - E F795 FCAL   | H & FORS FOR   | - K FIAS PCAL   | M & PTOS FCAL   | H K FORS FOR  | 4 K F 195 F CBL  | H 4 4735 FORL  | - E FING PAL  |  |
|--|--|---|--|---|---|---|--|--|---|--|
|  | 6 2 126 96<br>5 7 1765 1382<br>6 3 576, 549<br>6 3 692 697<br>6 3 466 664<br>7 6 661 673<br>6 1 356 166<br>9 3 734 235 | 7 6 77 76<br>8 6 328 305<br>8 6 57 56<br>6 5 39 113<br>7 5 316 316<br>8 5 72 106<br>8 5 160 128 | 4 5 224 214<br>4 5 123 133<br>7 5 23 <sup>5</sup> 224<br>9 6 53 29<br>7 7 116 14 <sup>8</sup><br>4 7 71 56 | 3 2 785 788<br>5 5 677 643<br>7 7 176 214<br>9 7 222 235<br>2 1 859 758<br>3 1 1227 1778<br>4 1 779 753 | 2 L 217 22C<br>4 L 1105 1054<br>• 1 268 25C<br>5 L 105 136<br>7 L 339 356<br>6 L 69 34<br>• 4 155 176 | 0 [ 14c [A0<br>2 2 2r+ 3)<br>3 1 723 574<br>5 2 397 523<br>7 2 397 157<br>3 3 777 75c<br>4 3 311 31*<br>8 3 574 538 | · · · · · · · · · · · · · · · · · · ·  | 7 L 207 515<br>8 L 163 144<br>1 2 63 57<br>2 2 725 57<br>1 3 2 127 115<br>6 2 443 455<br>7 2 176 92<br>6 2 366 328 | • • • • • • • • • • • • • • • • • • •                                   | 2 ^ >36 334<br>6 2 346 240<br>5 ^ 174 157<br>1 1 263 451<br>4 1 361 267<br>4 1 363 267<br>7 1 367 160<br>2 2 377 340 |
| 1 1 720 777<br>1 1 120 510<br>1 1 712 192  | 5 4 567 582<br>7 4 145 175<br>8 6 215 775  | 6 6 168 339<br>7 6 97 106<br>9 6 99 116   |  | 5 1 673 473<br>5 1 356 361<br>7 1 422 497   | 2 2 996 931<br>3 2 31 12<br>4 2 779 770   | • 3 333 35•<br>7 3 266 245<br>• 3 110 139   | 1 1 534 757<br>2 1 516 595<br>3 1 767 592  | 8 2 134 124<br>3 3 475 567<br>4 3 1°1 47   | 7 1 72 2°<br>~ 2 117 146<br>2 2 449 444                                 | - 2 765 234<br>- 2 764 176<br>- 3 165 336  |
| 4 47 71<br>4 57 71<br>5 1961 254<br>7 1 70 54<br>9 1 131 131<br>2 2 2247 7456              | 6 9 144 136<br>7 9 312 312<br>6 5 271 210<br>8 5 144 152<br>7 9 266 266  |   | 2 3 766 242<br>6 3 2176 2159<br>9 3 546 553<br>2 1 367 368<br>3 1 96 165                                   | 9 1 214 221<br>2 2 104 83<br>3 2 915 935<br>4 2 76 86<br>5 2 399 479                                    | b 2 192 205<br>3 3 720 735<br>4 3 152 140<br>5 3 549 551<br>6 3 159 155                               | 5 4 405 414<br>7 4 105 114<br>9 4 142 147<br>9 4 336 357<br>9 5 102 135   | 1 1 535 541<br>5 1 244 267<br>7 1 246 207<br>7 1 246 209<br>8 1 145 196          | 7 3 75 75<br>7 3 274 271<br>4 3 151 133<br>4 4 452 435<br>6 4 177 276  | 6 2 67 65<br>6 2 695 516<br>6 4 987 638<br>6 6 987 638<br>6 9 262 257   | 5 3 764 232<br>7 5 164 150<br>6 6 236 187<br>5 6 136 84<br>5 5 767 170   |
| 3 2 271 245<br>5 2 156 194<br>6 2 1335 1275<br>6 3 260 253<br>6 3 263 213                  | ······································   | 3 7 664 667<br>3 8 817 839<br>7 7 194 229<br>9 7 243 246  | 6 1 142 276<br>5 1 70 70<br>6 1 86 105<br>7 1 86 126<br>7 2 2673 2459                                      | 5 2 127 142<br>7 2 370 394<br>9 2 93 109<br>3 3 1729 1310<br>5 3 606 612                                | 7 3 507 337<br>8 3 106 173<br>9 3 218 208<br>6 9 92 911<br>9 6 99 112                                 | 7 5 178 207<br>9 5 155 152<br>7 6 179 256<br>7 6 179 256<br>7 121 116   | * 2 54% 564<br>6 2 143 74<br>6 7 272 514<br>7 2 267 274<br>8 2 47 50             | 5 4 197 155<br>5 5 752 755<br>7 5 152 145<br>6 6 206 196   | *********   | ******* 15*****  |
| 5 1 147 137<br>5 114 134<br>5 4 1571 1397<br>5 4 150 135<br>8 4 558 454                    | 7 1 1645 1747<br>• 7 1014 1021<br>• 7 614 601  | 2 L 121L 1243<br>6 1 643 234<br>5 1 421 423<br>6 L 603 6*2                                      | 5 2 120 117<br>6 2 71 99<br>7 2 54 16<br>5 2 1115 1127<br>7 2 97 78  | 6 3 627 377<br>7 3 284 327<br>3 3 164 176<br>9 3 196 167  | 7 • 50 70<br>• 256 277<br>5 5 145 329<br>• 5 L27 L1*  |   | 3 7 494 574<br>4 3 397 343<br>5 4 345 307<br>6 3 242 243<br>7 3 241 247          |  | 1 C 100 152<br>4 7 117 248<br>7 2 172 144<br>1 1 321 457<br>2 1 175 352 | 3 7 789 267<br>5 7 533 257<br>1 1 107 314<br>2 1 226 283<br>3 1 237 210  |
| 6 6 715 628<br>7 6 6 172   | - 7 446 415<br>2 1 304 766<br>3 1 1355 1240<br>4 1 147 174<br>5 1 744 752  | 7 1 241 255<br>9 1 241 255<br>9 1 230 219<br>2 2 97 34<br>3 2 1093 958                          | 3 2 34 15<br>3 3 60 26<br>6 3 160 112<br>5 1 127 57<br>6 3 103 156   | 5 4 367 401<br>6 4 66 52<br>7 6 147 145<br>6 4 197 193  | 7 3 276 276<br>8 5 54 83<br>9 5 87 152<br>8 8 702 332<br>8 8 85 89                                    | 4 0 1323 1370<br>8 0 470 470<br>1 1 276 114<br>2 1 47 114<br>3 1 42 32  | 4 3 101 171<br>4 3 167 193<br>4 4 340 343<br>7 4 40 116<br>7 5 230 253           | 7 7 311 246<br>5 7 415 700<br>7 7 135 121<br>8 7 157 147<br>2 1 414 437  | 3 1 354 2+2<br>4 1 357 271<br>5 1 267 334<br>6 1 278 147<br>7 1 174 14  | 6 1 224 263<br>5 1 271 160<br>5 1 117 124<br>7 1 127 111<br>5 2 244  |
|  | 7 1 916 911<br>9 1 132 159<br>9 1 236 229  | 4 2 375 374<br>5 7 45 53<br>7 7 439 436   | 9 3 83 97<br>4 4 1297 1266<br>5 4 136 133  | 6 5 174 100<br>7 5 254 240<br>7 5 771 137   | / / III IIV   | 6 1 100 174<br>5 1 67 57<br>6 1 175 166<br>7 1 66 57  | 5 5 143 157<br>7 5 142 199<br>8 5 126 144<br>7 6 155 159                         | * 1 424 441<br>* 1 357 352<br>5 1 354 376<br>* 1 122 232   | * 1 ** 114<br>3 2 380 320<br>8 2 234 711<br>* 2 138 144                 | 5 2 104 12"<br>7 2 19" 143<br>5 3 211 100<br>6 3 214 130   |
| 3 7 962 452<br>5 7 845 659<br>7 7 280 253<br>9 7 316 107<br>2 1 1170 1117<br>3 1 1477 1575 | 2 2 1949 1445<br>5 2 191 274<br>4 2 1765 1757<br>5 2 132 134<br>5 2 657 640  | 4 2 75 87<br>3 3 406 666<br>6 3 671 502<br>6 3 712 608<br>6 3 633 626<br>7 1 178 146            | 7 6 80 93<br>9 6 529 689<br>6 9 140 165<br>7 9 107 294<br>9 5 100 69                                       | 9 5 103 116<br>7 6 219 225<br>9 6 37 13<br>7 7 115 191<br>9 7 60 45                                     | j ( 741 723<br>5 ( 446 123<br>7 d 146 13  | 9 1 77 144<br>0 2 167 95<br>2 2 2119 1785<br>3 2 86 84<br>5 2 93 44   |  | 7 1 146 103<br>7 1 137 157<br>9 1 60 08<br>9 3 531 67<br>5 2 210 196   | 3 3 374 244<br>4 3 344 713<br>4 8 717 2*7<br>5 144 168<br>7 3 47 177    | 5 3 237 146<br>5 3 277 193<br>5 4 214 197  |
| 6 536 577<br>5 1 387 382<br>6 1 408 621  | 1 1 355 883<br>4 3 14C 136<br>7 1 52C 73C  | # 3 162 165<br># 3 216 106<br>6 6 132 137   | 6 6 510 563<br>7 6 56 55<br>9 5 66 16  |   | 9 0 203 23C<br>1 1 1335 1131<br>2 1 645 676   | 7 2 64 64<br>5 3 75 55<br>6 3 67 172  | 7 772 761<br>6 3 662 619<br>6 3 759 276  | 3 3 413 421<br>4 3 774 977<br>5 3 203 273  |   | ********  ******   |
| r 1 372 417<br>4 1 278 241<br>9 1 278 241<br>2 2 222 235<br>3 2 979 923<br>5 7 678 417     | - 1 177 138<br>- 3 327 338<br>- 4 107 104<br>- 3 254 275<br>- 4 101 155<br>- 4 027 425                                 |   |  | 2 ~ 1253 1254<br>4 C 1037 744<br>6 C 559 567<br>8 3 315 305   | • 1 •32 •30<br>• 1 •32 •30<br>• 1 •52 532<br>• 1 •27 324<br>7 1 326 373<br>• 1 260 233                | 6 6 821 367<br>5 6 86 46<br>8 6 313 357<br>6 9 426 626  | 217 24*<br>1 1 917 444<br>3 3 54* 616<br>4 1 92 95<br>5 1 456 451<br>4 1 115 127 | 6 3 210 238<br>7 5 161 176<br>8 6. 207 207<br>5 5 160 100<br>6 5 112 100<br>7 9 139 145                            | ********  | 3 5 144 124<br>4 5 444 444<br>5 144 54<br>2 2 441 54<br>2 2 441 54<br>2 3 35 54<br>4 4 44 744                        |
|  |  |   |  |   |   |   |  |  |   |  |

brated strip. The usual Lorentz-polarization factors were then applied to these intensities to yield  $F_0^2$ values where F<sub>o</sub> is the abserved structure factor amplitude. Appropriate corrections were made for absorption effects and the F<sub>o</sub> values were brought to an approximate scale through a modification of Wilson's procedure.<sup>2</sup> Using an absorption coefficient of 63.5  $cm^{-1}$ , we find the resultant transmission coefficients to range from 0.34 to 0.45.

Solution and Refinement of the Structure. A threedimensional Patterson function was calculated, but could not be interpreted assuming the molecular formula [Rh(Az)<sub>3</sub>I] with Z=4. A reformulation of the molecular formula to that of the six-coordinate Rh<sup>III</sup> complex [Rh(Az)<sub>4</sub>I<sub>2</sub>]I was then carried out and the positions of the Rh and I atoms were determined from the Patterson function. The Patterson function could only be interpreted assuming space group P4n2. The Rh atoms are located in the 2(d) special positions of the space group and thus the complex is crystallographically required to possess D<sub>2</sub> or 222 symmetry. The coordinated trans iodine atoms occupy the 4(g) special positions while the uncoordinated iodide ion is located in the 2(b) special position of P4n2.

The positional parameters of the rhodium and independent iodine atoms, along with variable isotropic temperature factors assigned to them, were refined through several cycles of least squares. The carbon and nitrogen atoms were then located in a difference Fourier based on phases obtained from the heavy atoms.

The structure was refined by a least squares procedure. The function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ where the weights w were assigned in the following way: I < 5, w = I/5;  $5 \le I \le 450$ , w = 1; I > 450,

w = 450/I, where I is the average raw intensity of the reflection. The neutral atom scattering factors which have been tabulated by Ibers<sup>3</sup> were used. The anomalous parts of the Rh and I scattering factors were obtained from Templeton's tabulation<sup>4</sup> and included in the calculated structure factors.5

In the initial rounds of calculations all atoms were assigned individual isotropic temperature factors. This refinement of positional, scale and thermal parameters converged to a conventional R factor (R = $\Sigma ||F_o| - |F_c|| / \Sigma ||F_o||$ ) of 0.090 and a weighted R factor  $R'(R' = (\Sigma w(|F_o| - |F_c|)^2) / \Sigma w F_o^2)^{1/2})$  of 0.092. After the above refinement in which scale factors were varied, a further refinement was carried out in which the scale factors were fixed, and the Rh and I atoms were allowed to vibrate anisotropically while the light atoms were restricted to isotropic vibration. This final refinement converged to a conventional R factor of 0.072 and a weighted R factor R' of 0.075. The observed and calculated structure factor amplitudes (in electrons  $\times$  10) are listed in Table I. An examination of Table I reveals that the reflections 400 and 220 probably suffer from the effect of secondary extinction but no extinction correction was made for the reflections. Positional, and isotropic and anisotropic thermal parameters are given in Table II.

Description of the Structure. The crystal structure of [Rh(Az)<sub>4</sub>I<sub>2</sub>]I consists of individual [Rh(Az)<sub>4</sub>- $I_2$ ]<sup>+</sup> cations and iodide anions. The structure of the cation is shown in Figure 1, and a stereo packing diagram is shown in Figure 2. The symmetry requires that the iodine atoms be trans. The coordination geometry about Rh is essentially a tetragonally distorted octahedron. The nitrogen atoms alternate 0.16 Å

<sup>(2)</sup> The computing for this structure determination was performed on Brown's IBM 360-50. The major programs used in this work were local modifications of Zalkin's FORDAP Fourier Program, the Busing-Levy ORFLS least-squares program, the Busing-Martin-Levy ORFFE function and error program and Johnson's ORTEP ellipsoid plot pro-gram. Other local programs were also used.

<sup>(3)</sup> J. A. Ibers, « International Tables for X-ray Crystallography » Kynoch Press, Birmingham, England, 1965, Vol. 3, Table 3.3.1 A.
(4) D. H. Templeton, *ibid.*, Vol. 3, Table 3.3.2 B.
(5) J. A. Ibers and W. C. Hamilton, *Acta Cryst.* 17, 781 (1964).

| Atom  |            | x                    | у                    | z                      |            | B, A <sup>2</sup> |
|-------|------------|----------------------|----------------------|------------------------|------------|-------------------|
| I2    | 0.0        | 000                  | 0.0000               | 0.500                  | 0          | _                 |
| Rh    | 0.5000     |                      | 0.0000               | 0.250                  | 0.2500     |                   |
| I     | 0.2        | 572 (2) <sup>a</sup> | 0.2428 (2)           | 0.250                  | 0          | _                 |
| Ν     | 0.3        | 84 (3)               | 0.146 (3)            | 0.155                  | (2)        | 3.2 (4)           |
| $C_i$ | 0.1        | 88 (4)               | 0.177 (4)            | 0.134                  | (3)        | 5.1 (7)           |
| C₂    | 0.2        | 85 (4)               | 0.078 (4)            | 0.073                  | (3)        | 5.9 (8)           |
|       |            | Ar                   | nisotropic Thermal P | arameters <sup>b</sup> |            |                   |
| I2    | 0.0208 (4) | 0.0208 (4)           | 0.0039 (2)           | 0.0000                 | 0.0000     | 0.0000            |
| Rh    | 0.0118 (3) | 0.0118 (3)           | 0.0034 (2)           | 0.0008 (4)             | 0.0000     | 0.0000            |
| I     | 0.0161 (2) | 0.0161 (2)           | 0.0059 (1)           | 0.0033 (3)             | 0.0010 (2) | -0.0010 (2)       |

Table II. Final Parameters for [Rh(Az),I<sub>2</sub>] I Positional and Isotropic Thermal Parameters

Table III. Internuclear Distances and Bond Angles in [Rh-(Az)₄I₂]I

| Interator                | mic Distances, Å     | Bond Angles, °           |                      |  |
|--------------------------|----------------------|--------------------------|----------------------|--|
| Rh—I<br>Rh—N             | 2.681 (5)            | N-Rh-I<br>N Rh I         | 94.5 (7)<br>85 5 (7) |  |
| $N-C_2$                  | 1.47 (4)             | N-Rh-N (cis)             | 76.3 (6)             |  |
| $N - C_1$<br>$C_1 - C_2$ | 1.58 (4)<br>1.36 (5) | N-Rh-N (trans)<br>Rh-N-C | 171 (1)<br>131 (1)   |  |
| I—N                      | 3.46 (2), 3.21 (2)   | $Rh - N - C_2$           | 126 (2)              |  |
|                          |                      | $N - C_1 - C_2$          | 60 (2)               |  |
|                          |                      | $N-C_z-C_1$              | 68 (3)               |  |



Figure 1. A stereoscopic view of the cation  $[Rh(Az)_4I_2]^+$ 



A stereoscopic drawing of the packing of the Figure 2.  $[Rh(Az),I_2]I$  complex as viewed approximately along the c axis.

above and below the equatorial plane drawn through the center of the rhodium atom and perpendicular to the iodine-rhodium-iodine bond axis. The ethylenimine rings are also staggered, being directed downward when the nitrogen atom is above the equatorial plane and upward when the nitrogen atom is below the plane. The interatomic distances, bond angles and their estimated standard deviations are listed in

Inorganica Chimica Acta | 3:3 | September, 1969

Table III. The rhodium-iodine bond distance of 2.681(4)Å is very similar to the Rh–I bond distance of 2.653(3)Å in  $[\pi - C_5 H_5 Rh(CO)(C_2 F_5)I]$ ,<sup>6</sup> and the Rh-I distance of 2.643(3)Å found in the square pyramidal complex  $[Rh((C_6H_5)_3P)_2I_2(CH_3)]$ .<sup>7</sup> However, the rhodium-nitrogen bond distance of 1.99(2)Å appears to be relatively short. For example, the five Rh-N distances in [Rh(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> are between 2.20 and 2.28 Å,8 and the Rh-N bond distance in the cation trans-[Rh(pyridine)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> is found to be 2.09 Å.<sup>9</sup>

Although the errors in the ethylenimine bond distances are large, it appears that the bond lengths in the complexed ethylenimine may be significantly different from those found for ethylenimine in the gas phase. The bond lengths observed for ethylenimine vapor are 1.488 Å for the C-N and 1.480 Å for the  $\hat{C}$ -C bonds.<sup>10</sup> The bond lengths for the ethylenimine rings in the cation  $[Rh(Az)_4I_2]^+$  are N-C<sub>1</sub> 1.58(4)Å, N-C<sub>2</sub> 1.47(4) and C<sub>1</sub>-C<sub>2</sub> 1.36(5)Å. A similar possible asymmetry in the coordinated ethylenimine ring has also been observed in the complex [Cu(Az)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>.<sup>11</sup>. In this complex the two C–N distances are 1.51(3)Å and 1.40(4)Å, and the C–C bond distance is 1.40(4)Å. The C–C bond distance in  $[Rh(Az)_4I_2]^+$  appears to be quite short at 1.36(5)Å, but the magnitude of the estimated standard deviation for this distance precludes any further conclusions concerning the electronic structure of the ligand or the complex.

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(6) M. R. Churchill, Inorg. Chem., 4, 1734 (1965). (7) P. G. H. Troughton and A. C. Shapski, Chem. Commun., 575

(1) P. G. H. Iroughton and A. C. Snepen, C. S. (1968).
(8) R. W. G. Wyckoff, « Crystal Structures », Vol. 3, 762 (1965).
(9) G. C. Dobinson, R. Mason, and D. R. Russel, *Chem. Commun.*, 62 (1967).
(10) T. E. Turner, V. C. Fiara, and W. M. Kendrick, *J. Chem. Phys.*, 23, 1966 (1955).
(11) Wan Bang Bang Ph. D. Thesis, Brown University, page 105 (10) 1. 2. (1955). (11) Won Bong Bang, Ph. D. Thesis, Brown University, page 105

<sup>&</sup>lt;sup>a</sup> Numbers in parentheses here and in the succeeding table represent the estimated standard deviations in the least significant figures. <sup>b</sup> The form of the anisotropic thermal ellipsoid is: exp  $\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$ .