Contribution from the Department of Chemistry,
Brown University Providence, Rhode Island 02912, U.S.A.

The Crystal and the Molecular Structure of *trans*-Diiodotetra(ethylenimine)rhodium(III) Iodide

R. Lussier, J. O. Edwards, and R. Eisenberg

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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 $P\bar{4}n2$ with a cell of dimensions* a = *7.81(1) Å,* c = *14.26(2) Å and V = 869.3 Å^3. The experimental density of 2.48 ± .04 g/cm^3 is consistent with a calculated value of 2.51 g/cm^3 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 octahedron. The ethylenimine nitrogen atoms alternate 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.[1] 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 π-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.*,[1] 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^{III} complex *trans*-$[Rh(Az)_4I_2]I$ 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.

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.*[1] 3 g of $[Rh(Az)_4Cl_2]Cl$ 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 $V = 869.3$ Å^3. 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 l for k+l odd, are consistent with the two acentric space groups $P\bar{4}n2$ (D_{2d}^8) and $P4_2nm$(C_{4v}^4). In addition, it was also observed that the reflections for which the sum h+k+l is even, were generally more intense than those for which h+k+l is odd.

An experimental density of 2.48 ± 0.04 g/cm^3 obtained by flotation in methylene chloride-methylene iodide solutions was not consistent with a calculated density 2.74 g/cm^3 for four molecules of $[Rh(Az)_3I]$ per unit cell. The observed density was, however, close to the value of 2.51 g/cm^3 calculated for two molecules of the closely related Rh^{III} complex $[Rh(Az)_4I_2]I$ per unit cell. The crystal morphology was C_{4v} with the {101} faces showing development. The volume of the crystal used for the collection of intensity data was calculated to be 6.0×10^{-3} mm^3.

Collection and Reduction of the Intensity Data. Intensity data were collected at room temperature by the equiinclination Weissenberg technique using Zr-filtered Mo K$_\alpha$ ($\lambda = 0.7107$ 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 $\Theta_{Mo} \leqslant 23.5°$ were estimated visually using a cali-

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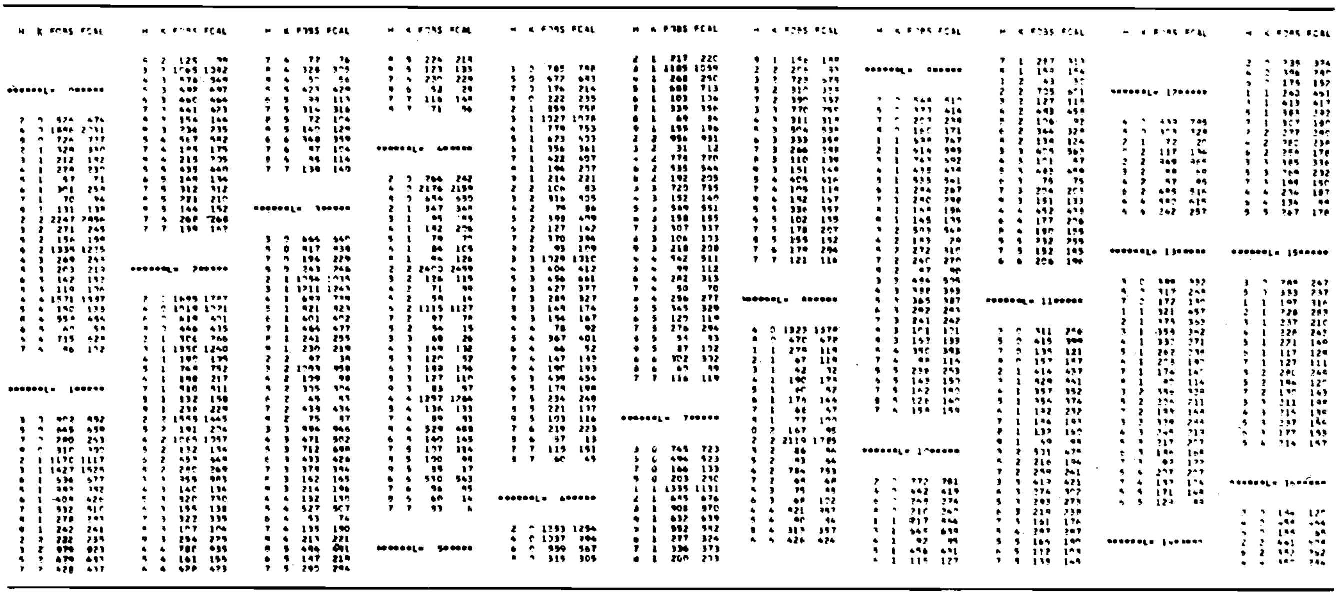
[1] J. Scherzer, P. K. Phillips, L. B. Clapp, and J. O. Edwards, *Inorg. Chem.*, *5*, 847 (1966).

Table I. Observed and Calculated Structure Factor Amplitudes (in electrons × 10) for $[Rh(Az)_4I_2]I$



brated strip. The usual Lorentz-polarization factors were then applied to these intensities to yield F_o^2 values where F_o is the observed structure factor amplitude. Appropriate corrections were made for absorption effects and the F_o values were brought to an approximate scale through a modification of Wilson's procedure.[2] 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 three-dimensional Patterson function was calculated, but could not be interpreted assuming the molecular formula $[Rh(Az)_3I]$ with $Z=4$. A reformulation of the molecular formula to that of the six-coordinate Rh^{III} complex $[Rh(Az)_4I_2]I$ 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 $P\bar{4}n2$. 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_2 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 $P\bar{4}n2$.

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: $I<5, w = I/5$; $5\leqslant I\leqslant 450, w = 1$; $I>450$, $w = 450/I$, where I is the average raw intensity of the reflection. The neutral atom scattering factors which have been tabulated by Ibers[3] were used. The anomalous parts of the Rh and I scattering factors were obtained from Templeton's tabulation[4] 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 $R'(R' = (\Sigma w(|F_o|-|F_c|)^2)/\Sigma wF_o^2)^{1/2})$ 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 × 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 $[Rh(Az)_4I_2]I$ consists of individual $[Rh(Az)_4I_2]^+$ 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

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(2) 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 program. Other local programs were also used.

(3) 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).

Table II. Final Parameters for $[Rh(Az)_4I_2]I$ Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, A^2
I_2	0.0000	0.0000	0.5000	—
Rh	0.5000	0.0000	0.2500	—
I	0.2572 (2) [a]	−0.2428 (2)	0.2500	—
N	0.384 (3)	0.146 (3)	0.155 (2)	3.2 (4)
C_1	0.188 (4)	0.177 (4)	0.134 (3)	5.1 (7)
C_2	0.285 (4)	0.078 (4)	0.073 (3)	5.9 (8)

Anisotropic Thermal Parameters [b]

I_2	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)

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

Table III. Internuclear Distances and Bond Angles in $[Rh(Az)_4I_2]I$

Interatomic Distances, Å		Bond Angles, °	
Rh—I	2.681 (5)	N—Rh—I	94.5 (7)
Rh—N	1.99 (2)	N—Rh—I	85.5 (7)
N—C_2	1.47 (4)	N—Rh—N (*cis*)	76.3 (6)
N—C_1	1.58 (4)	N—Rh—N (*trans*)	171 (1)
C_1—C_2	1.36 (5)	Rh—N—C_1	131 (1)
I—N	3.46 (2), 3.21 (2)	Rh—N—C_2	126 (2)
		C_1—N—C_2	53 (2)
		N—C_1—C_2	60 (2)
		N—C_2—C_1	68 (3)

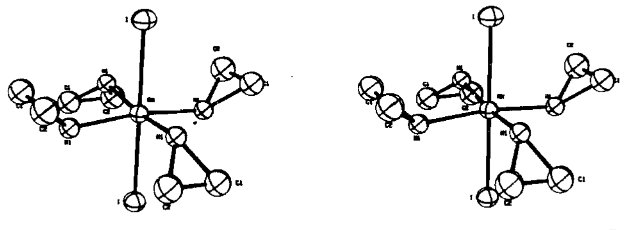

Figure 1. A stereoscopic view of the cation $[Rh(Az)_4I_2]^+$

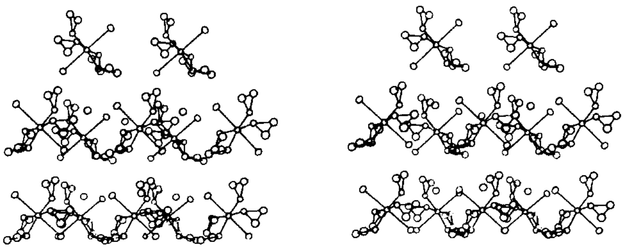

Figure 2. A stereoscopic drawing of the packing of the $[Rh(Az)_4I_2]I$ complex as viewed approximately along the c axis.

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 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 $[\pi\text{–}C_5H_5Rh(CO)(C_2F_5)I]$,[6] and the Rh–I distance of 2.643(3)Å found in the square pyramidal complex $[Rh((C_6H_5)_3P)_2I_2(CH_3)]$.[7] However, the rhodium-nitrogen bond distance of 1.99(2)Å appears to be relatively short. For example, the five Rh–N distances in $[Rh(NH_3)_5Cl]Cl_2$ are between 2.20 and 2.28 Å,[8] and the Rh–N bond distance in the cation *trans*–$[Rh(pyridine)_4Cl_2]^+$ is found to be 2.09 Å.[9]

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 C–C bonds.[10] The bond lengths for the ethylenimine rings in the cation $[Rh(Az)_4I_2]^+$ are N–C_1 1.58(4)Å, N–C_2 1.47(4) and C_1–C_2 1.36(5)Å. A similar possible asymmetry in the coordinated ethylenimine ring has also been observed in the complex $[Cu(Az)_4](NO_3)_2$.[11]. 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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