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The Bonding of Molecular Nitrogen. II. The Crystal and Molecular Structure of Azidodinitrogenbis(ethylenediamine)ruthenium(II) Hexafluorophosphate

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The crystal and molecular structure of the molecular nitrogen complex azidodinitrogenbis(ethylenediamine)ruthenium(II) hexafluorophosphate, $[\text{Ru}(\text{N}_3)(\text{N}_2)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2][\text{PF}_6]$, has been determined from three-dimensional X-ray data collected by counter techniques. The material is X-ray sensitive and it was necessary to use four different crystals for the data collection. The central metal atom is coordinated octahedrally to six nitrogen atoms. The Ru-N (of N_2) bond distance is 1.894 (9) Å and the Ru-N-N bond angle is 179.3 (9)°; the Ru-N (of N_3^-) bond distance is 2.121 (8) Å and the Ru-N-N bond angle is 116.7 (7)°. The Ru-N distances to the nitrogen atoms of the ethylenediamine groups range from 2.144 (9) to 2.108 (9) Å, with an average distance of 2.125 (19) Å. Crystal data: monoclinic, space group $C_{2h}^5-P2_1/n$; $a = 9.97$ (1) Å, $b = 12.01$ (1) Å, $c = 12.59$ (1) Å, $\beta = 102.4$ (3)°, $Z = 4$; $d_{\text{obsd}} = 2.00 \pm 0.03$ g/cm³, $d_{\text{calcd}} = 1.98$ g/cm³. The structure was refined using 1375 independent reflections from a limited data set for which $F^2 > 3\sigma(F^2)$, and the refinement converged to a conventional R factor (on F) of 5.6%.

Introduction

In the previously reported structure of $\text{CoH}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_3$,¹ we found that the Co-N bond is 1.807 (23) Å and by comparison with the Co-N distance of 1.936 (15) Å in $[\text{Co}(\text{NH}_3)_6]\text{I}_3$,² we concluded that, as expected, the metal-nitrogen (of N_2) bond has some multiple-bond character. In carrying out this present study of the bonding of molecular nitrogen, we chose azidodinitrogenbis(ethylenediamine)ruthenium(II) hexafluorophosphate because the central metal atom, ruthenium, was expected to be coordinated to three different types of nitrogen atoms. Thus we expected to obtain a direct, intramolecular comparison between a Ru-N single bond length and the length of the Ru-N bond when molecular nitrogen is the coordinating ligand. The compound is of further interest because it contains a coordinated azido group. Only a limited number of structures are known in which there is an azido group coordinated to a transition metal. This work bears directly on our previous studies of metal-nitrogen multiple bonds.³

Collection and Reduction of Intensity Data

The material is prepared⁴ by treating *trans*- $[\text{RuCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]\text{Cl}$ with silver *p*-toluenesulfonate and, after filtering, adding NaN_3 . This solution is allowed to stand and after several hours, a saturated solution of NaPF_6 is added. The crystals were kindly supplied by Dr. P. S. Sheridan. The N-N (of N_2) stretching frequency in this compound is 2103 cm⁻¹, at the lower end of the range 2105–2167 cm⁻¹ reported for the $\text{Ru}(\text{NH}_3)_5(\text{N}_2)^{2+}$ salts.⁵

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A series of Weissenberg and precession photographs taken with Cu $K\alpha$ radiation showed the crystals to be monoclinic with $2/m$ Laue symmetry. The systematic extinctions observed were: $h0l$ for $h + l$ odd and $0k0$ for k odd. These extinctions are consistent with the space group $C_{2h}^5-P2_1/n$.

A crystal was mounted, along the long dimension [100], in a thin-walled glass capillary for data collection on a Picker four-circle automatic diffractometer. It was observed that the material is extremely X-ray sensitive. The mosaic spread of the crystal, as determined by ω scans taken with a narrow source and open counter, increased greatly after only about 12 hr of exposure of the crystal to X-rays. This crystal was used to establish the following experimental conditions for data collection. The data were to be collected using Mo $K\alpha_1$ radiation (λ 0.7093 Å) and the diffracted beam was to be filtered through 3 mils of Nb foil. A takeoff angle of 2.2° would be used. At this takeoff angle, the peak intensity of a strong reflection was about 80% of the maximum value as a function of takeoff angle. The counter aperture selected was 4.0 mm \times 4.0 mm and was positioned 29 cm from the crystal. The pulse height analyzer was set for approximately a 90% window, centered on the Mo $K\alpha$ peak. The data were to be collected by the θ - 2θ scan technique at a scan rate of 1° in 2θ /min. An asymmetric scan range of 0.75° on the low-angle side and 1.25° on the high-angle side of the calculated 2θ values (Mo $K\alpha_1$) would be used. Stationary-counter, stationary-crystal background counts of 10 sec were to be taken at each end of the scan range. Attenuators were inserted automatically when the intensity of the diffracted beam exceeded 7000 counts/sec during the scan; the attenuators were Cu foil, their thicknesses being chosen to give attenuator factors of approximately 2.2. After these experimental conditions were determined, Friedel pairs of reflections (hkl and $\bar{h}\bar{k}\bar{l}$) were collected in the 2θ range 0–25°. These data were corrected for decomposition,

equivalent forms were averaged, and values of F_o^2 were derived. These were then used as input to a Patterson function calculation.

The rapid decomposition of this crystal indicated unusual sensitivity of the material to X-rays. Therefore, we had no choice but to collect data on several crystals. We will refer to these new crystals as I-IV. All crystals were mounted in thin-walled glass capillaries along the long dimension [100]. The experimental conditions described above were the same for data collection on each of the four crystals. In each case, the same ten reflections were centered on the diffractometer and used in a least-squares refinement of setting angles to determine cell constants,⁶ and the same three reference reflections (400, 040, 004) were used as a check on crystal decomposition. These reference reflections were measured every 100 reflections during the early stage of each run and every 50 reflections in the later stages. The cell constants, determined by methods previously described,⁶ are as follows (Mo $K\alpha_1$ radiation; λ 0.7093 Å): $a = 9.97$ (1) Å, $b = 12.01$ (1) Å, $c = 12.59$ (1) Å, $\beta = 102.4$ (3)°, at 22°. The details on each data set are given in Table I. The data in the

TABLE I
DETAILS OF DATA COLLECTION

Crystal no.	Dimensions, ^a mm	No. of observations ^b	2 θ range, deg	Av decompn. %
I	0.32 × 0.12 × 0.13	759	20-35	45
II	0.44 × 0.14 × 0.14	661	33.5-41	79
III	0.60 × 0.14 × 0.15	666	0-25 40-43	40
IV	0.64 × 0.10 × 0.12	600 ^c	42-49	55

^a Parallel to [100], [011], and [01 $\bar{1}$], respectively, of the parallelepiped-shaped crystals. ^b Owing to the problem of decomposition, only unique reflections were collected. ^c Although there were 882 reflections in this 2 θ range, owing to the weak intensity at higher 2 θ values coupled with decomposition, only 600 reflections were collected.

2 θ range 0-25° were recollected on crystal III because the crystal which was used for collection of Friedel pairs of reflections (hkl and $\bar{h}\bar{k}\bar{l}$) in this 2 θ range was first used for determination of the experimental conditions for data collection. We felt, therefore, that this crystal had severely decomposed even before data collection was begun and therefore we did not have an accurate measurement of decomposition on this early block of data. In general, all three standards decreased in intensity at approximately the same rate. A correction for decomposition was applied to each data set based on the average decomposition of the three standards as a function of X-ray exposure. Each block of data, with decomposition correction applied, was processed in the manner previously described,⁶ with a value of 0.04 for p selected for the calculation of $\sigma(I)$. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects. The data on the four

crystals were interscaled using common reflections.⁷ At first, all the data for which $I > 3\sigma(I)$ were used for interscaling and the interscaled data were used in the solution of the structure. We found, after solving the structure, that data from crystal II, which suffered the greatest average decomposition, were markedly inferior in the agreement between $|F_o|$ and $|F_c|$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. Therefore, the data were again interscaled using only crystals I, III, and IV. Of the resultant 1783 unique reflections, obtained by omitting data in the range $35 < 2\theta < 40^\circ$, only the 1375 which had $F^2 > 3\sigma(F^2)$ were used in the final refinement.

The absorption coefficient of this compound for Mo $K\alpha$ radiation is 11.9 cm⁻¹. On the basis of absorption correction tests,⁷ a correction for absorption proved unnecessary as the transmission factors did not vary by more than 1.5% for a given crystal.

Solution and Refinement

All least-squares refinements were carried out on F , the function minimized being $\sum w(|F_o| - |F_c|)^2$, where the weight w is taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c , the atomic scattering factors for the ruthenium and hydrogen atoms were those calculated by Cromer and Waber⁸ and by Stewart, Davidson, and Simpson,⁹ respectively; scattering factors for all other atoms were taken from the usual tabulation.¹⁰ The effects of anomalous dispersion of the ruthenium and phosphorus atoms were included in the calculation of F_o ;¹¹ the values of $\Delta f'$ and $\Delta f''$ used were those calculated by Cromer.¹²

The ruthenium atom and six nitrogen atoms coordinated to it were found from a Patterson function⁷ which was based on the data obtained on the initial crystal. These seven atoms were refined and structure factors were calculated. A difference Fourier synthesis revealed the phosphorus atom and provided no evidence of disorder problems. At this point we collected the data on crystals I-IV.

After the data from crystals I-IV were corrected for decomposition and interscaled, structure factors were calculated using the initial positions of the ruthenium, phosphorus, and six nitrogen atoms; this was followed by a difference Fourier synthesis. The positions of the six fluorine, four carbon, and the other three nitrogen atoms were found from this map. Three cycles of refinement were carried out in which the ruthenium and phosphorus atoms were refined with anisotropic thermal parameters, the six fluorine atoms were refined

(7) In addition to various local programs, Patterson functions and Fourier syntheses were calculated using a local version of Zalkin's *FORDAP*. Absorption correction tests were made by a modification of W. C. Hamilton's *GONO9* and data were interscaled using Hamilton's *INSCALE*. Refinement and structure factor calculations were done by our least-squares program, *NUCLS*, which, in its nongroup form, resembles the Busing-Levy *ORFLS*. Errors in derived quantities were obtained from the Busing-Levy *ORFFE* program, and drawings were made with use of Johnson's *ORTEP* program.

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TABLE II
 POSITIONAL AND THERMAL PARAMETERS FOR $[\text{Ru}(\text{N}_3)(\text{N}_2)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2][\text{PF}_6]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.22316 (8) ^b	0.16331 (7)	0.38589 (6)	0.00821 (10)	0.00482 (6)	0.00496 (6)	-0.00024 (7)	-0.00065 (5)	-0.00012 (6)
N1	0.4315 (9)	0.1792 (6)	0.3583 (7)	0.0130 (14)	0.0055 (7)	0.0054 (7)	-0.0011 (7)	-0.0000 (7)	-0.0001 (6)
C1	0.4626 (11)	0.0997 (9)	0.2782 (10)	0.0078 (13)	0.0080 (10)	0.0076 (10)	0.0001 (9)	0.0018 (9)	-0.0005 (8)
C2	0.3445 (13)	0.0981 (9)	0.1805 (9)	0.0142 (18)	0.0085 (11)	0.0048 (9)	-0.0008 (11)	0.0014 (10)	-0.0001 (8)
N2	0.2149 (10)	0.0737 (7)	0.2176 (7)	0.0130 (13)	0.0056 (7)	0.0055 (7)	-0.0012 (8)	-0.0021 (7)	-0.0002 (6)
N3	0.2329 (9)	0.2613 (7)	0.5064 (7)	0.0082 (11)	0.0077 (8)	0.0060 (7)	0.0006 (7)	-0.0014 (7)	-0.0013 (6)
C3	0.0935 (13)	0.2920 (11)	0.5177 (10)	0.0123 (18)	0.0097 (11)	0.0078 (10)	0.0010 (11)	0.0014 (11)	-0.0038 (9)
C4	-0.0014 (11)	0.1959 (10)	0.4798 (10)	0.0068 (13)	0.0095 (11)	0.0096 (12)	0.0024 (9)	0.0031 (10)	-0.0004 (9)
N4	0.0094 (9)	0.1824 (7)	0.3707 (7)	0.0095 (11)	0.0087 (7)	0.0068 (7)	-0.0007 (7)	0.0003 (7)	-0.0010 (6)
N5	0.1885 (8)	0.3134 (6)	0.2753 (7)	0.0107 (11)	0.0048 (7)	0.0057 (7)	0.0002 (6)	-0.0020 (7)	0.0003 (5)
N6	0.1047 (10)	0.3107 (7)	0.1935 (8)	0.0130 (14)	0.0061 (8)	0.0061 (8)	-0.0010 (7)	0.0002 (8)	0.0004 (6)
N7	0.0234 (11)	0.3084 (9)	0.1139 (8)	0.0174 (17)	0.0110 (11)	0.0072 (9)	-0.0015 (10)	-0.0027 (9)	0.0014 (8)
N8	0.2611 (9)	0.0314 (8)	0.4493 (7)	0.0120 (12)	0.0065 (8)	0.0048 (7)	0.0005 (7)	0.0021 (7)	-0.0002 (6)
N9	0.2828 (11)	-0.0453 (8)	0.4987 (9)	0.0216 (18)	0.0073 (9)	0.0091 (9)	0.0034 (10)	0.0039 (10)	0.0046 (8)
P	-0.1856 (4)	-0.0755 (3)	0.1773 (3)	0.0131 (5)	0.0087 (3)	0.0098 (3)	0.0012 (3)	-0.0011 (3)	-0.0017 (2)
F1	-0.0326 (8)	-0.0994 (6)	0.2389 (6)	0.0152 (12)	0.0118 (8)	0.0142 (9)	0.0014 (8)	-0.0042 (8)	-0.0021 (7)
F2	-0.3353 (9)	-0.0509 (8)	0.1146 (8)	0.0188 (13)	0.0140 (10)	0.0240 (12)	0.0051 (9)	-0.0117 (10)	-0.0050 (9)
F3	-0.2257 (12)	-0.1931 (8)	0.2100 (10)	0.0333 (22)	0.0125 (10)	0.0259 (16)	-0.0099 (12)	-0.0070 (13)	0.0039 (10)
F4	-0.1371 (12)	0.0405 (8)	0.1538 (10)	0.0351 (21)	0.0110 (9)	0.0270 (15)	-0.0042 (11)	-0.0118 (14)	0.0083 (10)
F5	-0.1553 (13)	-0.1282 (11)	0.0754 (8)	0.0355 (23)	0.0355 (20)	0.0108 (9)	0.0164 (17)	-0.0012 (12)	-0.0073 (12)
F6	-0.2100 (10)	-0.0268 (11)	0.2851 (9)	0.0243 (19)	0.0335 (19)	0.0187 (12)	0.0028 (15)	0.0073 (12)	-0.0124 (13)

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

as an octahedral group with an overall group thermal parameter, and the other atoms were refined with isotropic thermal parameters. At this time the contributions of the hydrogen atoms were calculated. Hydrogen atom positions for the two hydrogen atoms on each of the carbon and nitrogen atoms of the ethylenediamine groups were calculated from idealized tetrahedral geometry about the atom (C-H, N-H = 0.90 Å). The fixed contributions of the 16 hydrogen atoms to F_o were calculated using an isotropic thermal parameter of 5.0 Å² for each atom. Two cycles of refinement in which the six fluorine atoms were refined as a group with an overall group thermal parameter and all other atoms were refined with anisotropic thermal parameters gave agreement factors R_1 of 15.1% and R_2 of 18.0%, where $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and R_2 (or weighted R factor) = $(\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$. Structure factors were calculated and a statistical analysis indicated that the data from crystal II were inferior to the data from the other crystals.

Therefore, the data were scaled again, as described above, with the omission of those collected from crystal II. This resulted in a data set which omitted reflections in the range $35^\circ < 2\theta < 40^\circ$. The input parameters for the first cycle of refinement using this limited data set were those derived from the complete data set. After three cycles of refinement the positions of the 16 hydrogen atoms were recalculated and these were added as a fixed contribution to F_o . After three more cycles of refinement, in which all 21 atoms (ruthenium, phosphorus, six fluorine, four carbon, and nine nitrogen atoms) were refined anisotropically and data in the range $35^\circ < 2\theta < 40^\circ$ were omitted, convergence was reached at $R_1 = 5.6\%$ and $R_2 = 6.7\%$.

A statistical analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ and $\lambda^{-1} \sin \theta$ revealed no unexpected trends. In particular, no correction for extinction appeared necessary. The error in an observation of unit weight is 2.6 electrons.

The positional and thermal parameters derived from

the last cycle of refinement are presented in Table II along with the associated standard deviations in these parameters as derived from the inverse matrix. The idealized positional parameters of the hydrogen atoms of the ethylenediamine rings are listed in Table III.

 TABLE III
 DERIVED PARAMETERS FOR
 ETHYLENEDIAMINE HYDROGEN ATOMS^a

	<i>x</i>	<i>y</i>	<i>z</i>
N1H1 ^b	0.450	0.249	0.335
N1H2	0.488	0.167	0.423
C1H1	0.470	0.030	0.309
C1H2	0.542	0.115	0.260
C2H1	0.356	0.051	0.129
C2H2	0.333	0.170	0.149
N2H1	0.216	-0.002	0.230
N2H2	0.142	0.091	0.167
N3H1	0.272	0.223	0.568
N3H2	0.279	0.325	0.505
C3H1	0.090	0.308	0.589
C3H2	0.061	0.353	0.478
C4H1	-0.091	0.220	0.482
C4H2	0.019	0.141	0.529
N4H1	-0.038	0.212	0.320
N4H2	-0.028	-0.095	0.355

^a All atoms have $B = 5 \text{ \AA}^2$. ^b N1H1 and N1H2 are attached to N1, C1H1 and C1H2 are attached to C1, etc.

The final values of $10|F_o|$ and $10|F_c|$ (in electrons) are given in Table IV for the 1375 reflections which were used in the final refinement. For the 408 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, none had $|F_o^2 - F_c^2| > 4\sigma(F_o^2)$. Thus these data are not included in Table IV.

In principle there are no inherent dangers in dropping a block of data out of a least-squares refinement. If particular parameters are especially sensitive to data of that block, then marked increase in their resultant standard deviations will indicate this. Nevertheless, the procedure may not be a desirable one, as one is never dealing with an idealized least-squares procedure in which the observations suffer only from random

TABLE IV
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES X 10 (IN ELECTRONS)
FOR [Ru(N3)(N2)(NH2CH2CH2NH2)2][PF6]

Table with multiple columns (K, L, F, O, etc.) and rows of numerical data representing structure amplitudes. Includes sub-headers like 'OBSERVED' and 'CALCULATED'.

errors. In the practical experiment where observations are also subject to systematic errors it is more difficult to predict what effects on the derived parameters changes in the observations will have. In the present case it was very clear that the data collected from crystal II were inferior, probably because decomposition was most evident with this crystal. We could have dropped out the last quarter or perhaps half of the data block

where agreement was particularly poor, but this seemed to us to be too arbitrary. Accordingly since further data collection was not at that time feasible, we decided to drop the entire block of data. The fact that atomic parameters derived with or without the data from crystal II do not differ significantly adds support to the present essential, but perhaps undesirable, procedure.

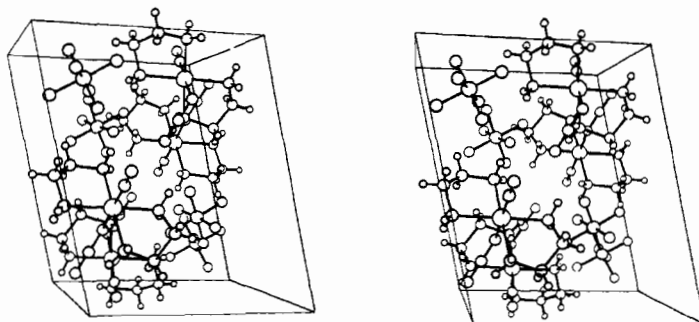


Figure 1.—A stereoscopic pair of views of the contents of a unit cell.

Description of the Structure

The structure consists of discrete PF_6^- and $\text{Ru}(\text{N}_3)(\text{N}_2)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2^+$ ions with no crystallographic symmetry imposed upon either. A stereoscopic pair of views of the contents of a unit cell is given in Figure 1. The closest, nonbonding contact of each of the amine hydrogen atoms is given in Table V. On the basis of

TABLE V
N-H...B INTERACTIONS AROUND CALCULATED
ETHYLENEDIAMINE HYDROGEN POSITIONS

B ^a	N ^a	H ^b	H...B, Å	N...B, Å	N-H-B ^c angle, deg
F1	1	1	2.28	3.18	167
N7	1	2	2.37	3.15	146
N5	2	1	2.43	3.27	153
F4	2	2	2.82	3.45	129
N7	3	1	2.48	3.04	120
F4	3	2	2.48	3.12	130
F3	4	1	2.57	3.29	135
F6	4	2	2.35	3.18	154

^a The numbering scheme of the cation is indicated in Figure 2. In the anion, F1 is trans to F2, F3 is trans to F4, and F5 is trans to F6. ^b The numbering scheme is as indicated in Table III. ^c All N-H distances were fixed at 0.90 Å.

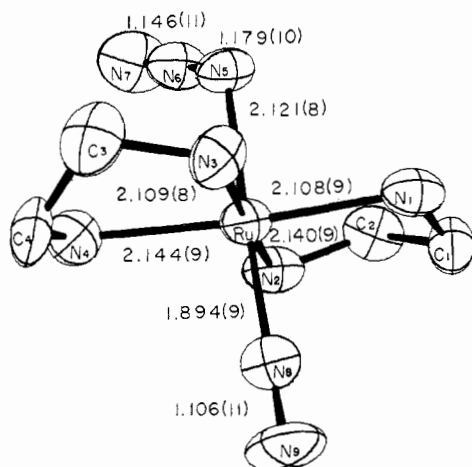


Figure 2.—An overall view of the cation.

structural data on N-H...F and N-H...N bonds,¹³ any such hydrogen bonds in this structure are very weak.

The coordination of the cation may be viewed in Figure 2. The ruthenium atom is octahedrally coordi-

nated by six nitrogen atoms. A selection of intramolecular bond distances and angles, together with estimated standard deviations as derived with the inclusion of correlation effects, is given in Tables VI and VII.

TABLE VI
INTRAMOLECULAR BOND DISTANCES

Atoms	Distance, Å	Mean distance, Å
Ru-N1	2.108 (9)	2.125 (19) ^a
Ru-N2	2.140 (9)	
Ru-N3	2.109 (8)	
Ru-N4	2.144 (9)	
Ru-N5	2.121 (8)	
Ru-N6	1.894 (9)	
N1-C1	1.470 (13)	1.474 (15)
N2-C2	1.495 (13)	
N3-C3	1.474 (13)	
N4-C4	1.458 (14)	
C1-C2	1.509 (14)	1.507 (14)
C3-C4	1.504 (15)	
N5-N6	1.179 (10)	1.162 (23)
N6-N7	1.146 (11)	
N8-N9	1.106 (11)	
P-F1	1.581 (8)	1.546 (24)
P-F2	1.560 (8)	
P-F3	1.548 (10)	
P-F4	1.524 (9)	
P-F5	1.517 (10)	
P-F6	1.545 (10)	

^a The standard deviation given for an average quantity in this table is that for an individual estimate as derived from the collection of values assumed to be equivalent or from an individual standard deviation, as obtained from the inverse matrix, whichever is the larger value. On this basis it appears that individual standard deviations derived from the inverse matrix are optimistic by a factor of 2.

TABLE VII
INTRAMOLECULAR BOND ANGLES

Atoms	Angle, deg	Mean angle, deg
N1-Ru-N2	81.9 (3)	81.6 (13)
N3-Ru-N4	81.2 (3)	
N2-Ru-N4	99.8 (3)	98 (2)
N1-Ru-N3	96.8 (3)	
Ru-N5-N6	116.7 (7)	109 (1)
Ru-N8-N9	179.3 (9)	
Ru-N1-C1	109.1 (6)	
Ru-N2-C2	107.5 (6)	109 (1)
Ru-N3-C3	110.3 (6)	
Ru-N4-C4	107.5 (6)	109 (1)
N1-C1-C2	108.9 (9)	
N2-C2-C1	108.8 (9)	
N3-C3-C4	108.6 (9)	110 (1)
N4-C4-C3	110 (1)	
N5-N6-N7	180 (1)	

(13) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

On the assumption that chemically equivalent bonds are indeed equal in length, it appears that these derived standard deviations are optimistic by a factor of approximately 2. The derived standard deviations are reliable if the data are subject only to random errors. Undoubtedly systematic errors have been introduced into the data as a result of decomposition and so we use twice these standard deviations as a basis for discussion. The root-mean-square amplitudes of vibration along the principal axes of vibration for atoms refined anisotropically are given in Table VIII. The directions of vi-

TABLE VIII

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å)			
Atom	Min	Intermed	Max
Ru	0.168 (1)	0.189 (1)	0.233 (1)
N1	0.189 (13)	0.204 (13)	0.268 (14)
C1	0.193 (16)	0.234 (16)	0.248 (16)
C2	0.191 (17)	0.245 (16)	0.268 (16)
N2	0.169 (13)	0.205 (13)	0.292 (13)
N3	0.165 (13)	0.223 (12)	0.270 (13)
C3	0.189 (19)	0.240 (17)	0.313 (16)
C4	0.155 (19)	0.269 (17)	0.276 (16)
N4	0.193 (13)	0.228 (12)	0.249 (13)
N5	0.167 (12)	0.189 (13)	0.275 (12)
N6	0.206 (14)	0.210 (12)	0.269 (14)
N7	0.200 (14)	0.273 (14)	0.344 (14)
N8	0.187 (15)	0.217 (13)	0.242 (12)
N9	0.161 (17)	0.290 (14)	0.339 (13)
P	0.210 (5)	0.225 (5)	0.320 (5)
F1	0.225 (11)	0.284 (10)	0.396 (11)
F2	0.208 (11)	0.296 (11)	0.540 (12)
F3	0.240 (12)	0.349 (12)	0.553 (14)
F4	0.232 (12)	0.319 (12)	0.592 (14)
F5	0.258 (13)	0.330 (12)	0.594 (16)
F6	0.255 (12)	0.359 (13)	0.551 (15)

bration of atoms in the cation may be discerned from Figure 2. Figure 2 also displays the numbering scheme employed for the cation.

The hexafluorophosphate anion is not unusual in any way. The six values of the P-F bond distance range from 1.517 (10)¹⁴ to 1.581 (8) Å to give a mean distance of 1.546 (24) Å. Owing to the large amount of thermal motion associated with the F atoms (Table VIII) this mean distance is necessarily shorter than the distance corrected for the effects of thermal motion. Such a correction does not appear to be feasible here, as the motion appears to be a combination of bond stretching, bond bending, and rigid-body torsional modes. Nevertheless, the mean distance is comparable with the P-F distance of 1.58 Å found in various PF₆⁻ salts.¹⁵ The F-P-F bond angles range from 87.0 (5) to 95.0 (8)°.

In the ethylenediamine group, the four C-N bond distances have a mean value of 1.474 (15) Å and the two C-C distances have an average value of 1.507 (14) Å. If we define the dihedral angle, α , as that angle between the normal to the plane which contains the metal atom and the ring carbon atoms and the normal to the plane which contains the metal atom and the ring nitrogen atoms, we would expect this angle to be nonzero for an

ethylenediamine ring in the gauche conformation. For the ring containing N1-C1-C2-N2, α is 27.6 (6)°, and for the ring containing N3-C3-C4-N4, α is 26.6 (7)°. These values compare well with the average value of 27° found in Cr(NH₂CH₂CH₂NH₂)₃³⁺.¹⁶ If the azido and molecular nitrogen groups are ignored and one looks at the plane containing the ruthenium atom and the two ethylenediamine rings, it is apparent that a pseudo-two-fold axis of rotation exists perpendicular to this plane. Upon rotation, C1 would go into C4 and C2 would go into C3. The weighted least-squares plane through these nine atoms is given in Table IX. It is found that

TABLE IX

WEIGHTED LEAST-SQUARES PLANE. EQUATION OF PLANE: 0.650x - 10.172y + 6.312z = 0.790 (MONOCLINIC COORDINATES)					
Atom	Dev from plane, Å	Atom	Dev from plane, Å	Atom	Dev from plane, Å
Ru	0.0027 (8)	C2	-0.426 (11)	C3	-0.432 (13)
N1	-0.072 (8)	N2	-0.027 (8)	C4	0.244 (12)
C1	0.252 (11)	N3	-0.101 (9)	N4	-0.097 (9)

C1 and C4 are approximately 0.2 Å above the plane and C2 and C3 are 0.4 Å below the plane. The N-Ru-N angle associated with the ethylenediamine groups is 81.6 (3)° owing to the "bite" of the ligand. The four Ru-N bond distances give a mean value of 2.125 (19) Å. As may be seen by comparison with various Ru-N bond lengths in Table X, the Ru-N bond length associated

TABLE X

SELECTED METAL-NITROGEN BOND LENGTHS

Compound	Bond type	Distance, Å	Ref
K ₂ OsNCl ₆	M≡N	1.614 (3)	a
ReNCl ₅ (P(C ₆ H ₅) ₃) ₂	M≡N	1.602 (9)	b
ReCl ₅ (NC ₆ H ₄ OCH ₃)(PC ₆ H ₅ (C ₂ H ₅) ₂) ₂	M=N	1.709 (4)	c
ReCl ₅ (NC ₆ H ₄ COCH ₃)(PC ₆ H ₅ (C ₂ H ₅) ₂) ₂	M=N	1.690 (5)	c
ReCl ₅ (NCH ₃)(PC ₆ H ₅ (C ₂ H ₅) ₂) ₂	M=N	1.685 (11)	d
K ₂ [Ru ₂ NCl ₈ (H ₂ O) ₂]	M=N	1.718	e
[Ru(NH ₃) ₆] ₂	M-N	2.144 (5)	f
[Ru(NH ₃) ₆](BF ₄) ₃	M-N	2.105 (4)	f
[Ru(NH ₃) ₅ N ₂ Ru(NH ₃) ₅](BF ₄) ₄	M-N	2.104 (6) (axial)	g
	M-N	2.12 (equatorial)	
	M=N	1.928 (6) (N ₂)	
[Ru(N ₂)(N ₂)(NH ₂ CH ₂ CH ₂ NH ₂) ₂](PF ₆) ₂	M-N	2.125 (19) (mean)	h
	M-N	2.121 (8) (azido)	
	M=N	1.894 (9) (N ₂)	

^a See ref 3. ^b R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). ^c D. Bright and J. A. Ibers, *ibid.*, **7**, 1099 (1968). ^d D. Bright and J. A. Ibers, *ibid.*, **8**, 703 (1969). ^e M. Ciechanowicz and A. C. Skapski, *Chem. Commun.*, 574 (1969). ^f H. Stynes and J. A. Ibers, unpublished results. ^g I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 6512 (1969). ^h This work.

with the ethylenediamine groups is in the range expected for a single-bond distance.

The coordinated azido group is of interest in this compound since relatively few structures are known in which this ligand is a ligand. These include coordination of the ligand to copper,¹⁷ cobalt,¹⁸ and iron.¹⁹ It appears

(14) For reasons discussed in the text, this number is more realistically 1.517 (20) Å, instead of 1.517 (10) Å.

(15) H. Bode and H. Clausen, *Z. Anorg. Chem.*, **265**, 229 (1951).

(16) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(17) I. Agell, *Acta Chem. Scand.*, **21**, 2647 (1967); Z. Dori, *Chem. Commun.*, 714 (1968); R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 738 (1970).

(18) G. J. Palenik, *Acta Crystallogr.*, **17**, 360 (1964).

(19) J. Drummond and J. S. Wood, *Chem. Commun.*, 1373 (1969).

TABLE XI
 BOND LENGTHS AND BOND ANGLES IN COORDINATED AZIDES

Compound	N-N, Å	M-N or H-N, Å	M-N-N, deg	Ref
HN ₃	1.240 (3)	1.02 (1)	112.65 (50)	<i>a</i>
N ₃ ⁻	1.134 (3)			<i>b</i>
	1.154 (15)			
(As(C ₆ H ₅) ₄) ₂ [Fe(N ₃) ₅]	1.16 (3)	2.041 (15) (axial) 1.971 (14) (equatorial)	124.8 125.1	<i>c</i>
[Co(N ₃)(NH ₃) ₅](N ₃) ₂	1.208 (7) 1.145 (7)	1.943 (5)	125.2 (2)	<i>d</i>
[Ru(N ₃)(N ₂)(NH ₂ CH ₂ CH ₂ NH ₂) ₂]PF ₆	1.179 (10) 1.146 (11) 1.163 (23) (mean)	2.121 (8)	116.7 (7)	<i>e</i>

^a E. Amkle and B. P. Dailey, *J. Chem. Phys.*, **18**, 1422 (1950). ^b B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959).
^c See ref 19. ^d See ref 18. ^e This work.

on the basis of the data in Table XI that if the azide is covalent, as in HN₃, the N-N bond lengths are not equal, but they are equal in an ionic azide, N₃⁻. The asymmetry of the azido group coordinated to a transition metal is open to question. In [Co(N₃)(NH₃)₅](N₃)₂,¹⁸ the azido group is asymmetric whereas in (As(C₆H₅)₄)₂[Fe(N₃)₅]¹⁹ the azido group is reported to be symmetric. In the present structure, the N-N distances do not differ significantly and average 1.162 (23) Å. The Ru-N bond distance associated with the azido group is that of an M-N single bond (M = metal), as has been found in other transition metal-azido complexes. The Ru-N-N bond angle is 116.7 (7)°, somewhat smaller than the M-N-N angle found in the other two complexes listed in Table XI.

The geometry of the coordinated molecular nitrogen is the same as that reported in other dinitrogen complexes. There is no significant lengthening of the N-N bond upon coordination, as may be seen by examination of the bond lengths listed in Table XII. The

 TABLE XII
 NITROGEN-NITROGEN BOND LENGTHS

Compound	Distance, Å	Ref
N ₂ (g)	1.098	<i>a</i>
CoH(N ₂)(P(C ₆ H ₅) ₃) ₃	1.112 (11)	<i>b</i>
[Ru(NH ₃) ₅ N ₂ Ru(NH ₃) ₅](BF ₄) ₄	1.124 (15)	<i>c</i>
[Ru(N ₃)(N ₂)(NH ₂ CH ₂ CH ₂ NH ₂) ₂]PF ₆	1.106 (11)	<i>d</i>

^a P. G. Wilkinson and N. B. Houk, *J. Chem. Phys.*, **24**, 528 (1956). ^b See ref 1. ^c See ref 22. ^d This work.

Ru-N bond length of 1.894 (9) Å is significantly shorter than an M-N single bond distance but not as short as an M=N bond distance, as seen by comparison with various M-N and M=N bond lengths listed in Table X and by comparison with the Ru-N bond distance of 2.121 (8) Å associated with the azido group and the mean distance of 2.125 (19) Å associated with the ethylenediamine groups found in this present study. The Ru-N distance is comparable with the mean Ru-C distances of 1.94 (3) and 2.01 (6) Å found in Ru₂(CO)₆Br₄²⁰ and Ru(CO)₄I₂,²¹ respectively. Therefore, as we have stated earlier, the bonding between a transition metal atom and molecular nitrogen is very similar to that between the metal and the isoelectronic ligand carbon monoxide. It is interesting that the N-N bond distance in this compound, as in CoH(N₂)(P(C₆H₅)₃)₃,¹ is not significantly shorter than the N-N bond length found in the bridging species [Ru(NH₃)₅N₂Ru(NH₃)₅](BF₄)₄.²²

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(20) S. Merlino and G. Montagnoli, *Acta Crystallogr., Sect. B.*, **24**, 424 (1968).

(21) L. F. Dahl and D. L. Wompler, *ibid.*, **15**, 946 (1962).

(22) I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 6512 (1969).