

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEXAS 76129

The Crystal and Molecular Structure of the Green Modification of Dichlorobis(4-methylpyridine 1-oxide)copper(II)

By D. R. JOHNSON AND W. H. WATSON*

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The crystal structure of the green form of dichlorobis(4-methylpyridine 1-oxide)copper(II), $(C_6H_7NO)_2CuCl_2$, has been determined by single-crystal X-ray diffraction techniques. Counter methods were used to collect 687 nonzero reflections. The complex crystallizes in the monoclinic space group $P2_1/c$ with two monomeric molecules per unit cell. The cell dimensions are $a = 6.28$ (1), $b = 10.663$ (5), $c = 11.453$ (5) Å, and $\beta = 101^\circ 45$ (10)'. The observed and calculated R densities are 1.57 and 1.56 g cm⁻³, respectively. The structure was refined by least-squares methods to a conventional R factor of 8.7%. The copper atoms lie at centers of symmetry and are coordinated to two chlorine and two oxygen atoms in a trans square-planar geometry. There is no close approach of atoms from adjacent monomers along the axial sites. The plane of the pyridine ring is at an angle of 93.9° with respect to the square plane about the copper ion. The terminal chlorine atoms do not interact with adjacent monomers, and the Cu-Cl stretching frequency of 339 cm⁻¹ should serve as a reference point for similar complexes.

Introduction

The 2:1 aromatic *N*-oxide complexes of copper(II) chloride can be divided into two general classes.¹ These two classes are (a) low and normal magnetic moment 2:1 dimeric complexes and (b) trans and distorted cis 2:1 monomeric complexes with normal magnetic moments.

The monomeric complexes of the group (b) type usually are characterized by two crystalline forms. These two forms may be identified by their green or yellow color. The infrared spectra of several 2:1 copper(II) chloride complexes of this type have been discussed by Hatfield and Whyman.² They indicate the green form exhibits metal-chlorine stretching modes at higher frequencies than the corresponding 1:1 complexes. In contrast, the yellow form absorbs at lower frequencies than the corresponding 1:1 complexes. The unit cell parameters and space groups, which were determined for several green complexes, indicated the complexes must have a trans square-planar geometry.³ The distance between copper(II) ions was too great for any significant chlorine-copper(II) intermolecular interactions as found in the 1:1 complex of di- μ -(pyridine 1-oxide)bis(dichlorocopper(II)).⁴ The higher metal-chlorine stretching frequencies observed in the infrared spectra of the green complexes reflect the presence of terminal metal-chlorine bonds, *i.e.*, structures containing chlorine atoms which do not interact with copper ions from neighboring molecules.

We wish to report the crystal and molecular structure of the green form of dichlorobis(4-methylpyridine 1-oxide)copper(II) as part of an investigation of the structural properties of *N*-oxide complexes. These studies were initiated to rationalize the chemical, magnetic, and optical properties of these systems in terms of their structures. A subsequent report will present the structure of the 2:1 yellow form of 4-methylpyridine 1-oxide.

Experimental Section

The 4-methylpyridine 1-oxide was obtained from Aldrich

Chemical Co. and was used without further purification. In general, mixing of ethanol solutions of the ligand with copper(II) chloride in a 2:1 mole ratio at room temperature yields only the 1:1 complex. The 2:1 complex is prepared by dissolving the 1:1 complex in boiling ethanol and adding a large excess of ligand. A mixture of yellow and green crystals is obtained by slow evaporation of the ethanol at room temperature. The green modification is the major product obtained under such conditions.

A dark green needle-shaped crystal with dimensions 0.357 × 0.150 × 0.167 mm was used in collecting all intensity data. The crystal was mounted with the long axis coincident with the spindle axis. The unit cell dimensions of the monoclinic crystal were determined at room temperature from a axis rotation and $0kl$ Weissenberg photographs, both calibrated with superimposed NaCl powder lines, $a = 5.6402$ Å. The photographs were obtained using zirconium-filtered Mo K α radiation (λ 0.71069 Å). The crystal data for $(CH_3C_5H_4NO)_2CuCl_2$, mol wt 352.7, are as follows: $a = 6.28$ (1), $b = 10.663$ (5), $c = 11.453$ (5) Å, $\beta = 101^\circ 45$ (10)'; systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$ (observed on $hk0$ and $h0l$ precession photographs and $0kl$ Weissenberg photograph); space group $P2_1/c$, (no. 14); $Z = 2$; $V = 750.7$ Å³; $\mu = 18.71$ cm⁻¹ (Mo K α); $d_{obsd} = 1.57$ g cm⁻³, $d_{calcd} = 1.56$ g, cm⁻³. The errors are standard deviations derived from the calculation of cell edges from a number of high-angle reflections or layer lines. The error in the angle is the average deviation obtained by several independent measurements of the same angle. The density was determined by the flotation method with a mixture of chloroform and bromoform.

Three-dimensional intensity data through the sixth level ($6kl$) were collected with a Philips Paired diffractometer using equiinclination geometry and a continuous ω -scan technique. The scan range varied from 2° for the zero level to 4° for the sixth level with a constant scan rate of 0.5°/min. Mo K α radiation and a silicon monochromator crystal [$d(111) = 3.1355$ Å] were used to collect all data. Several standard reflections were monitored throughout the data collection period. No change in intensity was observed. The monitored reflections are used to scale the levels together, and this scaling is checked several times during the structure refinement. In general, all of the nonequivalent reflections of the type hkl and $h\bar{k}l$ were collected up to a 2θ limit of 50.8°. For the zero level, where $0kl = 0k\bar{l}$, the equivalent reflections were averaged to give one unique set of data. A total of 1406 nonequivalent intensities were measured, and 687 were tabulated as having an observed intensity. If the recorded intensity was greater than twice the calculated standard deviation for the reflection, the intensity was classified as observed.

The raw data were reduced to structure factors using a standard data reduction program with Lorentz and polarization corrections applied to the data.⁵ Standard deviations were assigned to the structure factors on the basis of counting statistics. Included in the standard deviation is an instrument instability term which

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 (3) M. R. Kidd, R. S. Sager, and W. H. Watson, *ibid.*, **6**, 946 (1967).
 (4) R. S. Sager, R. J. Williams, and W. H. Watson, *ibid.*, **8**, 694 (1969).

(5) A listing and description of all programs may be found in the Ph.D. dissertation of N. R. Stemple, Texas Christian University, 1970.

was chosen as 3% of the magnitude of the observed raw intensity. The standard deviation is given by

$$\sigma(F_o) = \frac{1}{2} \frac{1}{\sqrt{Lp}} \sqrt{\frac{N_B + RN_B + (0.03I_o)^2}{I_o}}$$

$$I_o = N_B - RN_B$$

where N_B is the total count obtained during a scan cycle, N_B is the total background count, R is a constant which relates the background count time to the total scan time, and I_o is the number of counts associated with each reflection. If a cylindrical shape is assumed for the crystal, the maximum error that could be introduced by ignoring absorption corrections was found to be 4%. Therefore, no absorption corrections were made to the data. The scattering factors of Cromer and Waber⁶ were used for all nonhydrogen atoms. The hydrogen scattering factors were those of Stewart, Davidson, and Simpson.⁷ The scattering factors for copper and chlorine atoms were corrected for the real part of the anomalous dispersion using the values of Cromer.⁸

Structure Determination

Since there are two molecules per unit cell, space group considerations require the copper atoms to lie at centers of symmetry at the positions (0, 0, 0) and (0, $\frac{1}{2}$, $\frac{1}{2}$). The position of the chlorine atom was determined from a Patterson map. Calculation of the structure factors using the coordinates of the two heavy atoms yielded $R = 0.41$ for the 687 observed reflections, where $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$.

A three-dimensional Fourier map was calculated using the phases assigned on the basis of structure factor calculations, and all of the remaining non-hydrogen atoms were located. Reflections having $F_o > 2F_c$ were omitted in the calculation of the Fourier map. Structure factors calculated using the positional coordinates of all the atoms yielded an R factor of 0.24.

A full-matrix least-squares refinement was carried out using the positional parameters from the Fourier map. Initially, all atoms were assigned isotropic temperature factors consistent with those obtained for other N -oxide structures.^{4,9-12} Three cycles of refinement yielded $R = 0.088$ for 360 of the strongest observed reflections. The copper atomic position was fixed in each refinement cycle. The weighting scheme used in the refinement was $w = 1/\sigma(F_o)^2$. In later refinement, those reflections assigned a zero observed magnitude were assigned zero weight.

Anisotropic temperature factors were assigned to the copper, chlorine, oxygen, and methyl carbon atoms, and the refinement was continued. The ring hydrogen atomic positions were included in the structure factor calculation, but they were not refined. The hydrogen positions were determined by a program which assumes they are in the plane of the ring at a distance of 1.08 Å from the carbon atoms. Nine cycles of refinement yielded $R = 0.062$ and $R(\text{WTD}) = 0.042$, where $R(\text{WTD}) = \frac{\sum w ||F_o| - |F_c||}{\sum w |F_o|}$, for the 508 reflections which had $w > 0.60$. Addition of the anisotropic temperature factors was determined to be significant at the $\alpha = 0.005$ level based on Hamilton's

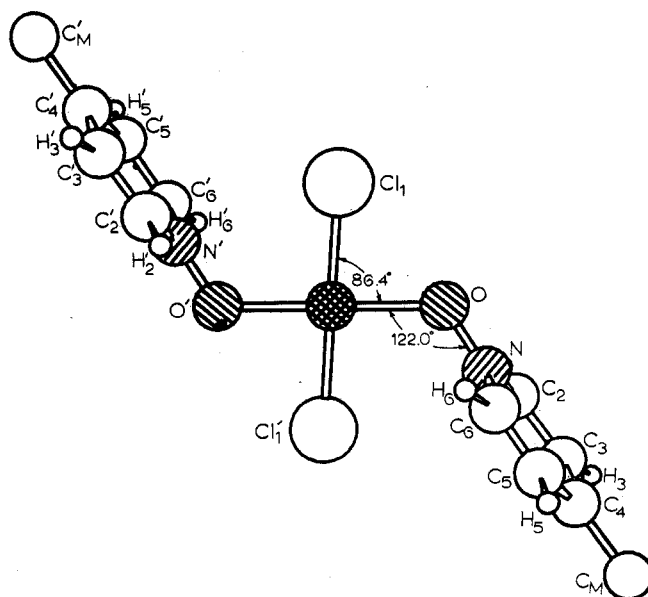


Figure 1.—A projection of the structure of *trans*-dichlorobis(4-methylpyridine 1-oxide)copper(II) onto the square plane containing the copper(II) ion.

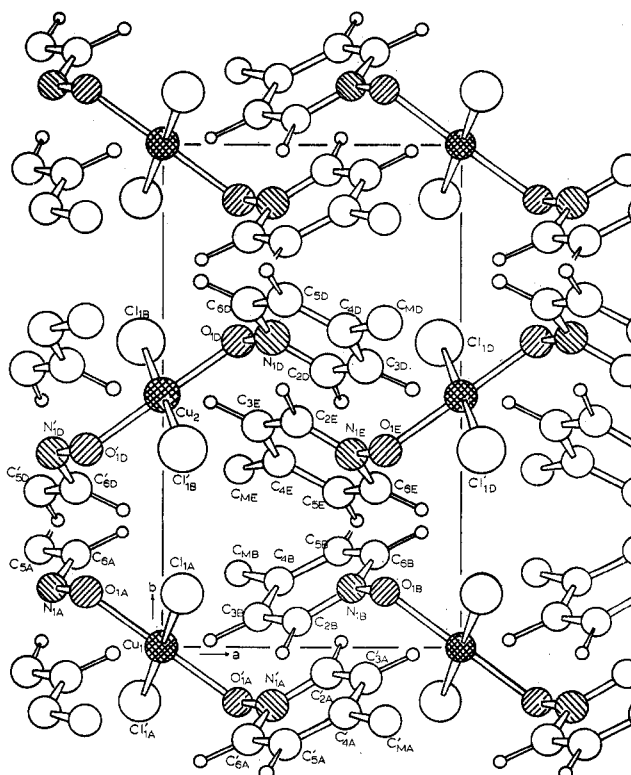


Figure 2.—A projection of the structure of *trans*-dichlorobis(4-methylpyridine 1-oxide)copper(II) onto the ab plane.

significance test of the change in R factor during refinement.¹³

After the last cycle of refinement, the largest shift was less than one-seventh the estimated standard deviation of the parameter. The estimated standard deviations were calculated from the inverse of the normal-equations matrix. A structure factor calculation using the final positional parameters yielded $R = 0.087$ for the 687 observed reflections. The ob-

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TABLE I
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $(C_6H_7NO)_2CuCl_2$

Table with 14 columns representing observed and calculated structure factors (K, L, |F_o|, |F_c|) for various reflections. The table is a grid of data points corresponding to different hkl reflections.

served and calculated structure factors are listed in Table I. Those reflections initially assigned a zero magnitude generally were found to have a calculated magnitude less than the minimum observed magnitude of 8.0. The final positional, isotropic, and anisotropic thermal parameters and their estimated standard deviations are listed in Table II.

A final three-dimensional difference Fourier showed no peaks larger than $0.4e^-/\text{\AA}^3$, which indicated the absence of solvent molecules. Small peaks were observed about ring carbon atom positions and indicated anisotropic vibrations for these atoms. There were no distinguishable peaks about the methyl carbon,

and assignment of the methyl hydrogens was not possible.

Discussion

A projection of the complex onto the square plane containing the copper(II) ion is shown in Figure 1. Projection of the unit cell contents along the *c* axis is shown in Figure 2. The molecules are monomeric, and a trans square-planar geometry about the copper(II) ion is evident. The term trans square planar is used because the bond angles are approximately 90°; however, the Cu-Cl bonds (2.227 Å) are longer than the Cu-O bonds (1.949 Å) as expected. Bond distances

TABLE II
 ATOMIC AND THERMAL PARAMETERS FOR DICHLOROBIS(4-METHYLPYRIDINE 1-OXIDE)COPPER(II), GREEN MODIFICATION

Atom	x^a	y	z	B or B_{11}^b	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0000	0.0000	0.0000	2.9 (1)	3.4 (1)	1.9 (1)	-1.3 (3)	0.7 (1)	-0.3 (3)
Cl	0.0699 (5)	0.1064 (3)	0.1710 (2)	4.0 (2)	5.0 (2)	3.2 (2)	1.5 (3)	-1.0 (3)	-1.9 (3)
O	-0.2537 (12)	0.1086 (6)	-0.0456 (5)	4.6 (4)	6.0 (5)	1.4 (3)	3.3 (8)	-1.2 (7)	-2.1 (6)
N	-0.3667 (15)	0.1154 (8)	-0.1584 (8)	2.8 (2)					
C(2)	-0.5502 (16)	0.0504 (9)	-0.1882 (9)	3.5 (3)					
C(3)	-0.6798 (17)	0.0594 (9)	-0.3008 (10)	4.0 (3)					
C(4)	-0.6097 (18)	0.1297 (10)	-0.3907 (10)	3.9 (3)					
C(5)	-0.4089 (19)	0.1910 (10)	-0.3537 (9)	3.7 (3)					
C(6)	-0.2869 (17)	0.1826 (10)	-0.2388 (9)	3.5 (3)					
C(M)	-0.7442 (22)	0.1462 (9)	-0.5202 (9)	7.6 (9)	5.4 (7)	0.9 (5)	3.0 (13)	-4.9 (11)	1.9 (9)
H(2)	0.402	0.012	0.877	2.0					
H(3)	0.163	0.013	0.681	2.0					
H(5)	0.653	0.249	0.583	2.0					
H(6)	0.871	0.228	0.784	2.0					

^a Numbers in parentheses are estimated standard deviations of the last significant digits. ^b Anisotropic thermal parameters have the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}k lb^*c^*)]$. ^c Hydrogen parameters were used to calculate structure factors but were not refined.

 TABLE III
 INTERACTOMIC DISTANCES AND BOND ANGLES IN DICHLOROBIS(4-METHYLPYRIDINE 1-OXIDE)COPPER(II), GREEN MODIFICATION^a

Bond Lengths, Å			
Cu-Cl	2.227 (3)	N-C(6)	1.34 (1)
Cu-O	1.949 (6)	C(2)-C(3)	1.38 (1)
N-O	1.34 (1)	C(3)-C(4)	1.41 (1)
N-C(2)	1.33 (1)	C(4)-C(5)	1.41 (1)
Shortest Nonbonding Distances, ^b Å			
Cl(1A)-Cl(1A')	4.455 (4)	Cl(1D')-C(5C)	3.66 (1)
O(1A)-O(1A')	3.898 (7)	Cl(1D')-C(6C)	3.47 (1)
O(1A')-Cl(1A')	2.867 (6)	Cu(1)-C(2B)	3.919 (9)
O(1B)-C(5E)	3.35 (1)	Cl(1A')-C(3B)	3.575 (9)
Cu(1)-C(2A')	3.715 (9)	Cl(1A)-N(1A')	3.027 (9)
Cu(1)-C(6A')	3.535 (9)	Cl(1A)-C(2A')	3.413 (9)
Cl(1A)-O(1A')	3.050 (7)		
Bond Angles, Deg			
Cl-Cu-O	86.4 (2)	C(2)-N-C(6)	121.7 (9)
Cu-O-N	122.0 (5)	N-C(2)-C(3)	121.3 (9)
O-N-C(2)	118.7 (8)	C(2)-C(3)-C(4)	120.4 (8)
O-N-C(6)	119.6 (8)	C(3)-C(4)-C(5)	115.3 (9)
		C(4)-C(5)-C(6)	123.6 (9)
		C(5)-C(6)-N	118.3 (8)
		C(3)-C(4)-C(M)	124.3 (9)
		C(5)-C(4)-C(M)	120.5 (9)
		C(5)-C(6)	1.37 (1)
		C(4)-C(M)	1.56 (1)
		Cl(1A)-C(6A')	3.389 (9)
		Cl(1B')-C(MB)	3.76 (1)
		Cu(2)-C(MB)	4.11 (1)
		Cl(1B')-C(4B)	3.61 (1)
		Cl(1B')-C(3B)	3.88 (1)
		Cl(1B')-C(5B)	3.97 (1)

^a Numbers in parentheses are estimated standard deviations. ^b Atom numbering notation used in Figure 2.

and angles, as well as important nonbonding distances, are given in Table III.

The observed bond lengths are consistent with the bond lengths reported for other structures of this type.^{4,9-12} The structure of pyridine *N*-oxide was reported recently,¹⁴ and the bond lengths in the ring system are equivalent to those reported in this work within the calculated standard deviations. The average of four C-C bond lengths is 1.393 Å, and the N-C bond lengths are 1.33 and 1.34 Å. The N-O bond length of 1.34 Å is consistent with a reduction of the double-bond character due to complex formation. The Cu-O bond length of 1.949 Å is shorter than the Cu-O distances found in the bridged complexes of pyridine *N*-oxide (1.98 and 2.04 Å)⁴ and 2-picoline *N*-oxide (1.98 and 2.01 Å).¹⁰ The formation of an additional Cu-O bond in the bridged complexes reduces the strength of the individual bonds. The Cu-Cl bond distance of 2.227 Å is normal for a bonded nonbridging chlorine. All of the bond angles observed in the ring system are near 120° except for the C₃-C₄-C₅ angle which is compressed to 115.2°.

There is no indication of intermolecular bonding or association of the copper atoms along the axial direction perpendicular to the square plane. The closest inter-

molecular approach of this nature is with a methyl carbon of an adjacent monomer which lies at 4.11 Å. All of the intermolecular distances are consistent with ordinary van der Waals interactions.

A least-squares plane fitted to the pyridine ring yielded the equation $-0.541x + 0.799y + 0.262z - 2.337 = 0$. The average deviation of the six ring atoms from the plane is 0.014 Å. The maximum deviation from the plane is 0.028 Å for the C₂ atom. This distance is within two standard deviations of the estimated deviation from the plane. Thus, the ring is planar within experimental error. The oxygen atom is 0.052 Å out of the ring plane, which indicates the N-O bond is bent from the plane by 2.2°. The methyl carbon atom is displaced from the ring plane in the same direction as the oxygen by 0.059 Å, which indicates the C₄-C_M bond also is bent from the plane by 2.2°. The slight distortion of the oxygen from the ring plane has been noted in other complexes of pyridine *N*-oxide.^{9,10} The distortion of the methyl carbon from the plane is related to the compressed C₃-C₄-C₅ bond angle. The square-planar portion of the molecule can be described by the equation $-0.645x - 0.653y + 0.398z - 1.927 = 0$. The para carbon atom of the ring (C₄) is 0.77 Å out of the square plane, and the methyl carbon atom is 1.11 Å out of this plane. A line passed through the nitrogen and para carbon atoms

(14) J. C. Morrow, presented at the National Meeting of the American Crystallographic Association, New Orleans, La., March 1970.

makes an angle of approximately 11° to the square plane.

The Cl-Cu-O bond angle is 86.4° , which is close to the expected value of 90° . The distortion from 90° is a consequence of the repulsive interaction of the chlorine atom and the pyridine portion of the ligand which causes the Cl'-Cu-O angle to expand. The Cu-O-N angle also is expanded to 122.0° as a result of this interaction. The dihedral angle between the normal to the square-planar plane and the normal to the pyridine ring plane is 93.9° with the C₆ atom tilted toward the copper. This orientation of the ring minimizes intramolecular steric interactions of the ortho hydrogens with the chlorine atoms. The stability of several monomeric complexes with filled d orbitals has been rationalized in terms of back- π -bonding.^{15,16} Back- π -bonding is not effective in this

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complex. The electron-donating nature of the 4-methyl substituent raises the energy of the π -anti-bonding orbital which would participate in back- π -bonding, and the steric effect would dominate.

The Cu-Cl vibration at 339 cm^{-1} is associated with a free terminal chlorine atom, and the frequency should serve as a reference for these vibrations. The green trans form is the thermodynamically stable isomer, and a minimum steric interaction is found. Inter-molecular interactions are hindered along the axial direction of the square plane by the perpendicular orientation of the pyridine ring. A small solvent molecule can occupy these sites and adducts are formed readily.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

The Structure of Bis(trifluorophosphine)diborane(4), Determined by Electron Diffraction

BY E. R. LORY, R. F. PORTER, AND S. H. BAUER*

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The gas-phase structure of bis(trifluorophosphine)diborane(4) has been determined by electron diffraction. The trifluorophosphine groups are trans about the boron-boron axis, with the phosphorus and boron atoms coplanar. The B-B distance is $1.800 \pm 0.036\text{ \AA}$, B-P = $1.848 \pm 0.028\text{ \AA}$, and P-F = $1.539 \pm 0.003\text{ \AA}$. These are similar to the corresponding parameters found in trifluorophosphine-borane. The position of the hydrogen atoms could not be uniquely determined, but the data favor a structure with four terminal hydrogen atoms rather than a structure in which two of the hydrogen atoms form a bridge. The matrix-isolation infrared and gas-phase Raman spectra are consistent with a molecule which has a center of symmetry.

Introduction

Although diborane(4) has not been isolated, several of its bis adducts have been prepared.¹⁻⁴ Spectroscopic data suggest that the adducts do not contain bridging hydrogen atoms while their chemical properties indicate the presence of a boron-boron bond. However, no structural studies have been made on any member of this class of compounds. This is a report on a gas-phase electron diffraction determination of the molecular structure of bis(trifluorophosphine)diborane(4), B₂H₄(PF₃)₂; the conclusions are supported by infrared and Raman spectra.

Experimental Section

A sample of bis(trifluorophosphine)diborane(4) was prepared² and purified by glpc. The sample tube, fitted with a Teflon needle valve, was connected directly to the nozzle lead tube of the electron diffraction apparatus. The sample was held at -65° (vapor pressure 8 Torr) while the photographs were taken. The ambient pressure in the diffraction apparatus during sample

injection was 2×10^{-6} Torr. Sected electron diffraction photographs were taken (acceleration voltage 60.62 kV) for 35 sec using the long nozzle-to-plate position (25.6 cm) and for 60 sec using the short nozzle-to-plate position (12.4 cm). Procedures used in this laboratory for measuring plates and reducing the diffraction data have been described.⁵⁻⁷

The gas-phase Raman spectrum of the compound was recorded on a Spex-Ramalog spectrometer using a CRL 52MG laser as the excitation source.⁸ The 488-nm argon line was multipassed through a cylindrical Pyrex cell (volume 23 cm³) which held the sample (at a pressure of 10 cm and argon as a diluent at 20 cm). The cell was maintained at -196° until immediately prior to recording the spectrum, to minimize sample decomposition.

The matrix-isolation infrared spectrum was recorded with a Perkin-Elmer 521 spectrometer. The argon sample mixture (500:1) was deposited on a CsI window held near 5°K , at a rate of 10 mmol/hr.

Results

The reduced scattered intensity as a function of angle is shown in Figure 1 [$q = 8-127\text{ \AA}^{-1}$, $q \equiv (40/\lambda) \sin(\theta/2)$]. The refined radial distribution curve,

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(8) Spectrum recorded by Dr. J. Allkins, Spex Industries, Metuchen, N. J.