THE CRYSTAL AND MOLECULAR STRUCTURE OF 2,2'BIPYRIDYLGLYCINATOCHLORO COPPER(II) DIHYDRATE

THESIS

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The three-dimensional x-ray structure of 2,2'-bipyridyl-glycinatochloro copper(II) dihydrate has been fully refined to a final R factor of 0.081. The bipyridyl and glycine ligands are arranged about the central copper atom in a square planar configuration while the chlorine atom is 2.635 angstroms above this plane directly over the copper atom. This unusually long distance is explained by the positioning of a glycine group on the opposite side of the square plane, resulting in a distorted octahedral arrangement. Also, the chlorine atom is linked to three oxygen atoms via hydrogen bonding, thus stabilizing the distorted octahedral complex.

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CHAPTER I

INTRODUCTION

It has been known for some time (8) that $3d^9$ copper(II) octahedral and square planar complexes undergo considerable Jahn-Teller (9) distortions. These distortions produce respectively distorted octahedral and distorted tetrahedral structures (1). Dutta and associates observed that the magnetic moments of several $3d^9$ copper(II) heterochelates in aqueous solution are approximately 1.90 Bohr Magnetons (5), indicating the presence of an unpaired electron (4, p. 537).

2,2'-Bipyridiylglycinatochloro copper(II) dihydrate (BPGC) absorbs at 16,940(5)* to 15,880(5) cm^{-1} in the ultraviolet region (5, p. 354). For a system with one free electron in its d orbitals, transitions in the ultraviolet region are expected to peak out at a wave-number of approximately 10,000 (4, p. 572). This is true also of the d^9 system. The absorption band of copper(II) in aqueous media is complex and the bands tend to consist of many peaks over a rather scattered range, which is indicative of Jahn-Teller distorted systems (2; 4, p. 572). Most copper(II) compounds

*Here and elsewhere in this manuscript, the standard error or estimated deviation will be specified in parenthesis following the parameter value. The digits of this number correspond to the least-significant digits of the parameter.

exhibit such extreme distortions that they are best described as distorted square planar. The distortions most frequently occur along the dz^2 axis (6, p. 322).

A comparison of some copper(II) pyridine bonded systems is shown in Table I. It should be noted that the square planar and octahedral complexes are distorted. Huheey has compiled a table of bond distances for Jahn-Teller distorted copper(II) complexes, part of which is shown in Table II (7, p. 325). From the table, it can be seen that, for octahedral distorted structures, certain bond lengths differ dramatically. These deviations could be, in some cases, explained by arguments consistent with the Jahn-Teller theorem.

Using this information, it is possible to say tentatively that BPGC will be distorted from an octahedral or tetrahedral structure. Merritt found that short hydrogen-hydrogen contacts produced steric interaction, thereby resulting in distortions (11). The bonding sights for dipyridine in all cases observed have been at the nitrogen positions. The glycine molecule can bond at either oxygen or nitrogen positions, or both.

From this information, it is possible to obtain several chemically acceptable structures of BPGC. The crystal structure of this compound was attempted in order to observe

TABLE I

BOND LENGTHS (Å) AND COORDINATION STRUCTURE OF SOME COPPER(II) COMPLEXES CONTAINING PYRIDINE

Copper(II) Coordination Structure	Cu - N	Cu - O	Cu - Halide
Trigonal Bipyramid (13)	2.04, 2.01 2.07, 1.99	2.30	-------
Trigonal bipyramid (17)	1.98, 2.11 2.07, 1.96	2.05	-------
Trigonal bypyramid (2)	2.03, 2.10 1.96, 2.00	----	2.70
Square planar distorted (15)	1.98, 1.98	----	2.25
Square planar distorted (15)	1.98, 1.98	----	2.39
Square planar distorted (16)	1.98, 1.98	1.99, 1.99	-------
Octahedral distorted (12)	1.98, 2.02 1.97, 1.99	2.45, 2.73	-------
Octahedral distorted (6)	1.98, 2.02	1.98, 1.95 2.40, 2.40	-------
Octahedral distorted (10)	2.00, 2.00	1.92, 1.92 2.38	-------
Octahedral distorted (3)	1.98, 1.98 2.03, 2.03	2.72, 2.72	-------

TABLE II

METAL-LIGAND DISTANCES OF SOME COPPER(II) COMPLEXES*

Compound	Short Distances (Å)			Long Distances (Å)
	Cu-Cl	Cu-O	Cu-N	Cu-Cl
$CuCl_2$	2.30 2.30 2.30 2.30			2.95 2.95
$CsCuCl_3$	2.30 2.30 2.30 2.30			2.65 2.65
$CuCl_2 \cdot 2H_2O$	2.28 2.28	1.93 1.93		2.95 2.95
$CuCl_2 \cdot 2C_5H_5N$	2.28 2.28		2.02 2.02	3.05 3.05
$Cu(NH_3)_2Cl_2$			1.95 1.95	2.78 2.78 2.78 2.78

*Table from Huheey (7)

effects of Jahn-Teller distortions on the copper coordination as well as the types, if any, of hydrogen bonding.

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CHAPTER II

EXPERIMENTAL

Deep blue, long prismatic crystals of BPGC (1) were obtained from A. Syamal of the Department of Chemistry, North Texas State University, Denton, Texas. The crystals were recrystallized in a slightly basic aqueous solution in order to reduce the crystalline size to a suitably small size for the General Electric manual diffractometer. Flotation methods indicated a crystal density of approximately 1.55 g cm^{-3}. Using four molecules per unit cell, the actual calculated density is 1.665 g cm^{-3}. These crystals were examined with the aid of a polarizing microscope, and several optically suitable crystals were selected. Single oscillation photographs revealed, after several tried, a non-twinned crystal. The crystal chosen was approximately 0.30 x 0.42 x 0.25 mm in size. The crystal was mounted along the long axis, later designated as the b axis, in an effort to minimize absorption problems. From the oscillation and Weissenberg photographs, the cell geometry was determined to be monoclinic. It was determined from the systematic absences of reflections,

0k0 absent when k is odd,

h0l absent when l is odd,

that the unit cell is of the centric space group $P2_1/c$ (3). Easy alignment on the General Electric XRD manual diffractometer was possible due to the fact that the crystal was mounted along the b axis giving a plane of reflection at a chi (χ) of 90° and any setting of phi (ϕ).

Using cell constants calculated from Weissenberg photographs, preliminary settings of two-theta (2θ), χ, and ϕ were calculated for twelve reflections in the 2θ range of between 0.00° and 23.00°. The intensities were maximized for these reflections, none of which were in the zero layer, and the settings of χ, ϕ, and 2θ were recorded. Subsequently, these settings were used to refine the unit cell constants through a least squares fit of the original settings to the settings calculated from the indices. These results are shown in Table III.

Using the unit cell constants thus obtained, a new set of reflection settings was generated to a 2θ of 60°. Intensity data were collected, using the peak height method. Molybdenum $K\alpha_1$ radiation ($\lambda = 0.70926$ Å) was used with a zirconium filter. The x-ray tube was operated at 40,000 volts and twenty milliamps. The takeoff angle on the x-ray tube was 2.00°. Originally, data were taken using a forty second peak top count and two background counts of twenty seconds each. This procedure was modified to a twenty second peak top count and ten second background counts after approximately twenty percent of the data had been

TABLE III

THE EXPERIMENTAL AND CALCULATED CELL CONSTANTS FOR THE MONOCLINIC UNIT CELL OF BPGC

Cell Constants	Film Data	Least Squares Fit Data
A	10.473 Å	10.474(3) Å
B	18.525	18.507(13)
C	7.723	7.724(6)
β	103.87°	103.918(59)°

taken. This modification was made due to the excessive time being consumed in data collection. Initially, the (800) reflection was used as a standard. When counting time was reduced, it was decided to add a thicker zirconium filter. This modification reduced the (800) standard to below 1000 counts per twenty second timing period; therefore, a new standard, the (830) reflection was chosen. The standard was measured at the end of each fifteen intensity collections. When the standard reflection intensity began to fluctuate over ten percent, data collection was stopped for that day under the assumption that the diffractometer power supply stability was beginning to vary with increasing temperature. All data were collected using the same crystal.

The raw data were interpolated between standards and then corrected for peak spreading as 2θ increased. The

constants used to account for peak spreading were empirically determined by graphing as the abscissa,

$$\frac{\text{SCANNED INTENSITY} - 6(\text{FIXED BACKGROUND})}{\text{FIXED INTENSITY} \_ \text{FIXED BACKGROUND}},$$

and 2θ as the ordinate for numerous reflections along the entire 2θ range. A least squares best line was drawn through these points and the constant values taken from this line. This graph is shown in Figure 1. There were initially 3649 reflections, ranging through a 2θ of 55°.

The data thus obtained were multiplied by 0.9 to minimize computation errors. The resultant intensities, I_{obs}, were corrected for Lorentz and polarization effects (6, p. 196), which led to the observed structure factor, F_{obs}, for each hkl reflection. The structure factors were put on an absolute basis by the equation,

$$|F_{abs}| = K|F_{obs}|$$

where K is the scale factor calculated by the statistical methods of Wilson (5) and $|F_{abs}|$ is the observed structure factor scaled to an absolute basis. In the Wilson method, a value for K is obtained from the equation,

$$\ln \frac{I_{obs}}{\sum f_{o_i}} = \ln \frac{1}{K^2} - \frac{2B\sin^2\theta}{\lambda^2}$$

where B is the overall isotropic temperature factor and f_{o_i} is the atomic scattering factor for the ith atom. This latter quantity is summed over all N atoms in the unit cell. B and K are determined from the slope and intercept,

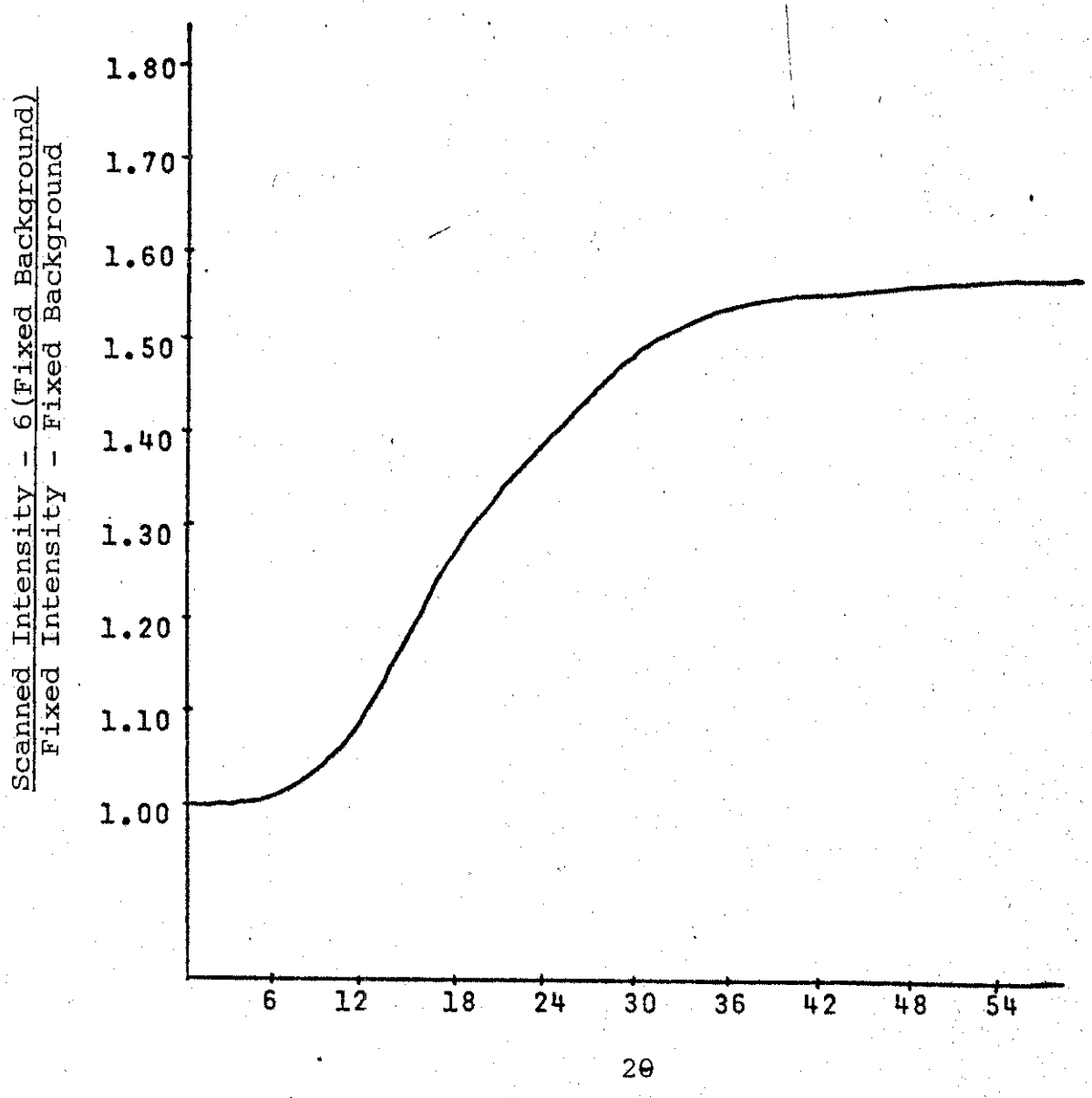

Fig. 1--Graph of correction constants for BPGC used to correct for peak spreading as 2θ increases.

respectively, of the Wilson plot. The values of B and K were found to be 3.20 $\AA^2$ and 0.7645, respectively.

Normalized structure factors, E's, were computed according to the equation (5),

$$E = \frac{KF_{obs} \exp\left[B(\sin\theta/\lambda)^2\right]}{\epsilon \sum_{i=1}^{N} f_{oi}^2}$$

The factor ϵ is a statistical factor determined by symmetry which allows for the fact that reflections which are systematically absent have average intensities which are integral multiples of the average of the general reflections (6). For the space group $P2_1/c$, ϵ is equal to two for h0l and 0k0 reflections, and equal to one for all other reflections. The experimental values for the E distribution are found in Table IV. This again confirms the centric space group.

TABLE IV

THE EXPERIMENTAL DISTRIBUTION OF E VALUES FROM DIFFRACTOMETER INTENSITY DATA FOR BPGC COMPARED WITH THE THEORETICAL CENTRIC AND ACENTRIC DISTRIBUTIONS

E Value Distribution	Experimental	Theoretical (Centric)	Theoretical (Acentric)
Average magnitude of E	0.814	0.798	0.886
Average magnitude of E^2	1.003	1.000	1.000
Average magnitude of (E^2-1)	0.931	0.968	0.736
Percentage of E values greater than 1.00	32.86	32.00	37.00
Percentage of E values greater than 2.00	4.59	5.00	1.80
Percentage of E values greater than 3.00	0.26	0.30	0.01

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CHAPTER III

STRUCTURE DETERMINATION AND REFINEMENT

It has been shown that when a molecule possesses an atom which comprises approximately thirty percent of the total molecular weight of the molecule, heavy atom methods are preferred over a direct method solution. Heavy atom methods were used to determine the structure of BPGC due to the fact that the copper composition is approximately twenty-one percent.

At this point, in the absence of knowledge of the signs of the structure factors, it was not possible to deduce directly the actual positions of atoms contained within the unit cell. However, it is theoretically possible to deduce the interatomic vectors between the atoms. It has been shown by Patterson (1) that a Fourier synthesis, using the values of the observed structure factors squared, as Fourier coefficients, will produce a density map which yields the coordinates of the ends of these vectors according to the equation (1),

$$\rho(u,v,w) = \frac{1}{V}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} \left|F_{obs}(h,k,l)\right|^2 \cos 2\pi(hu + kv + lw).$$

Here, $\rho(u,v,w)$ represents the magnitude of an interatomic vector peak at the point (u,v,w). If one considers the

fact that groups of atoms are spherically symmetric (9), implying complete scattering, then the calculated structure factor has the equation

$$F_{calc} = \sum_{j=1}^{N} f_j \exp(2\pi i S \cdot r_j).$$

Here, r is the position vector of atom j and is mathematically defined as $hx_j + ky_j + lz_j$. S is the reciprocal lattice point at which the function is evaluated. One can derive the square for the structure factor by simply multiplying the factors together for the peak involved. For two atoms, j and k, the vectors r_j and r_k enter into the relation

$$\left|F_h\right|^2_{i,n} = \sum_{j=1}^{N} \sum_{k=1}^{N} f_j f_k \exp(2\pi i S \cdot (r_k - r_j)),$$

where $\left|F_h\right|^2_{i,n}$ represents a structure in which "atoms" of scattering factors $f_j f_k$ are located at $r_k - r_j$ (10, p. 228).

In 1936, Harker showed that for three-dimensional Patterson maps certain symmetry related conveniences were present (4). These conveniences were restricted to structures possessing certain symmetry operators (10, p. 232). For the BPGC monoclinic system, the Harker sections correspond to the P2/m point group (7). The P2/m symmetry lacks the glide plane and screw axis required for $P2_1/c$.

Using Harker symmetry points, it was possible to find the copper coordinates, from which a set of structure

factors was calculated according to the equation (7)

$$F_{calc} = \sum_{j=1}^{N} f_j^o \cos 2\pi (hx_j + ky_j + lz_j) \exp(-B \sin^2\theta/\lambda^2).$$

In the above equation, f_j^o is the atomic scattering factor at zero degrees kelvin for the j'th atom and the exponential term is the temperature correction for isotropic vibration. The scattering power curves were obtained from the averaged set of scattering curves in the International Tables for X-ray Crystallography (7, pp. 216-227).

Having obtained the calculated structure factors (F_{calc}) and the previously defined observed structure factors (F_{obs}), it was possible to calculate the residual index (R). This index,

$$R = \frac{\sum_{i=1}^{N} \left| |F_{obs}| - |F_{calc}| \right|}{\sum_{i=1}^{N} |F_{obs}|}$$

where i represents an individual reflection and N represents the total number of reflections, is a measure of the reliability of a proposed structure solution. It has been shown (11, p. 372) that the theoretical statistical residual index should have the following values for centric and acentric random structures:

$$R_{random,centric} = 0.83$$

$$R_{random,acentric} = 0.59.$$

Using only the copper atom found from the Patterson

synthesis, the residual index was 0.568. This index value was below the theoretical random centric value.

This copper position was refined isotropically through a block diagonal least squares, minimizing the quantity

$$\sum_{h,k,l} w(h,k,l)\ \left(\left|F_{obs}(h,k,l)\right|^2 - \left|k\ F_{calc}(h,k,l)\right|^2 \right)^2$$

where k is a factor scaling the F_{calc} to the F_{obs}. This method of refinement (4) allows the inclusion of "accidentally absent" reflections which are too weak for observation. Usually, the minimum observed structure factor can be estimated in the part of the spectrum where the reflection resides. Thus, in a centrosymmetric space group, such a $P2_1/c$, the expected observed structure factor for the reflection can be estimated as (1) 0.5 F_{obs}min and its variance estimated as $\alpha^2 = 0.08\ F_{obs}$min, where F_{obs}min is the minimum observable structure factor. In the above equation, w is represented as $w = \alpha^{-2} = 12 / (F_{obs}\text{min})^2$.

One cycle of least squares isotropic refinement produced calculated structure factors which were used to produce an electron density map, using the equation (6, p. 329)

$$\rho(x,y,z) = \frac{4}{V} \left(\sum_{h,k,l}^{k+l=2N} [A - B] + \sum_{h,k,l}^{k+l=2n+1} [D - C] \right)$$

where $\rho(x,y,z)$ is the electron density at the point (x,y,z) and $A = [F(h,k,l) + F(h,k,\bar{l})] \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz$,

$B = [F(h,k,l) - F(h,k,\bar{l})] \sin 2\pi hx \cos 2\pi ky \sin 2\pi lz$,

$C = [F(h,k,l) - F(h,k,\bar{l})] \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz$, and

$D = [F(h,k,l) - F(h,k,\bar{l})] \cos 2\pi hx \sin 2\pi ky \sin 2\pi lz$.

From the electron density map produced, two nitrogen and one oxygen atom were located. Subsequent isotropic least squares refinement produced more precise coordinates for these atoms which led to a residual index of 0.413. The electron density map produced from these coordinates revealed the positions of one oxygen atom and twelve carbon atoms. Once again, an isotropic least squares refinement was carried out and resulted in a new residual index of 0.28.

At this point, a difference Fourier map was calculated using the equation (12, p. 356)

$$\Delta \rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l (F_{obs} - F_{calc}) \cos 2\pi (hx + ky + lz),$$

where $\Delta\rho(x,y,z)$ represents the difference between the density calculated with the observed magnitudes and the trial structure (3, p. 198). This method revealed one more oxygen atom which, when included in an isotropic least squares cycle, lowered the residual index to 0.26.

At this point, six cycles of anisotropic block diagonal least squares calculations were performed on the structure resulting in a lowering of the residual index to 0.154. The calculated structure factor expression for anisotropic temperature factors is given in the expression

$$F_{calc_r} = \sum_r f_r^{\circ} \cos \left[2\pi(hx_r + ky_r + lz_r)\right] \exp(-C_r)$$

(12, p. 450), where C_r is defined as

$$C_r = B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{23}kl + 2B_{13}hl + 2B_{12}$$

for the r^{th} atom. In the above equation, f_r^o is the atomic scattering factor at zero degrees kelvin and the exponential term is a correction for the anisotropic thermal vibration.

Using the calculated and observed structure factors, a graph was constructed of $\sin^2\theta$ verses relative index for all data collected. From the graph, it was possible to determine that the data were inconsistent above forty-five degrees in 2θ. The computer program used as an aid in generating Figure 2 is contained in the appendix.

Using the forty-five-degree cutoff point reduced the number of usable reflections to 1896. Seven cycles of anisotropic refinement reduced the residual index to 0.101. At this point, theoretical atomic positions for the hydrogen atoms were calculated for the rings, as well as the tetrahedral positions (3). The hydrogen atoms coordinated to the two free water oxygen atoms were not determined. The temperature factors for the hydrogen atoms were the same as those for the atoms to which they were coordinated; however, they remained fixed during refinement. The hydrogen atomic positions were included in the refinement, but were not allowed to vary. An additional three anisotropic refinements reduced the residual index to 0.091. With the change in the atomic positions of the non-hydrogen atoms,

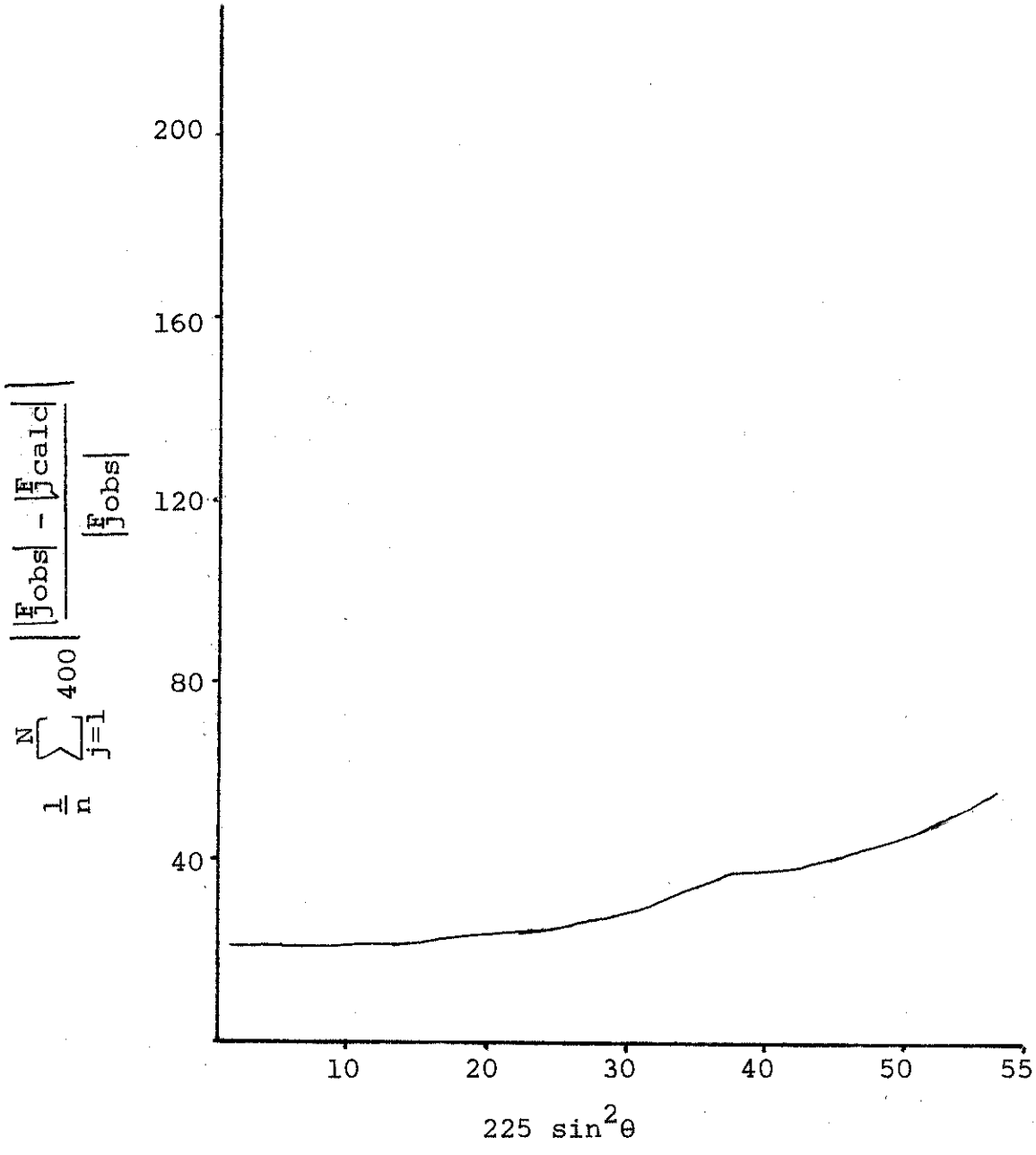

Fig. 2--The graph of relative index verses $\sin^2\theta$ required to choose a data cutoff point.

it was necessary to recalculate the hydrogen positions. Using these new hydrogen positions, one last structure factor calculation resulted in a final residual index of 0.081.

The final atomic and thermal parameters for BPGC are listed in Table V. A listing of the final observed and calculated structure factors for the 1896 reflections used is given in Table VI.

TABLE V

FINAL ATOMIC AND THERMAL PARAMETERS OF THE CRYSTAL STRUCTURE OF BPGC

Atom	Fractional Coordinates X 10^5		
	x	v	z
Cu	13724(14)	8656(8)	32998(21)
Cl	5819(32)	17508(18)	5809(47)
O(1)	-1780(69)	2380(69)	28201(110)
O(2)	78371(75)	1034(49)	33829(118)
O(3)	26719(90)	38262(50)	35056(127)
O(4)	85258(113)	25980(64)	22973(154)
N(1)	24339(81)	1606(47)	22446(119)
N(2)	31456(86)	13577(51)	40760(126)
N(3)	4982(86)	13920(51)	50080(134)
C(1)	19540(108)	-4250(67)	12910(166)
C(2)	27740(117)	-9400(68)	7340(165)
C(3)	41180(121)	-7980(71)	11970(177)
C(4)	46100(106)	-0164(68)	21640(169)
C(5)	37389(104)	2950(62)	26473(147)
C(6)	41289(105)	9932(59)	36345(148)
C(7)	54146(105)	12548(67)	40872(169)
C(8)	56440(112)	19076(70)	48709(181)
C(9)	46412(127)	22790(69)	52700(187)
C(10)	33925(123)	19946(69)	48396(184)
C(11)	-8910(115)	11340(67)	46526(194)
C(12)	-11260(113)	4446(68)	35219(164)
H(1)	90355	44903	40610
H(2)	76044	35829	50127
H(3)	84710	15540	39493
H(4)	44128	49570	25017

TABLE V--Continued

Atom	Fractional Coordinates X 10^5		
	x	y	z
H(7)	61852	9295	38016
H(8)	65667	21304	51808
H(9)	48167	22052	9235
H(10)	26414	23034	51348
H(11)	88667	10271	59083
H(11)	53499	38230	41857
H(N)	9831	37206	13169
H(N)	5177	30546	-2040

	Anisotropic Temperature Factors X 10^5					
	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Cu	387(15)	172(5)	1797(35)	-32(16)	795(36)	-193(25)
Cl	905(41)	198(12)	2166(87)	19(37)	961(96)	156(53)
O(1)	353(86)	226(32)	2410(225)	-238(86)	803(222)	-406(138)
O(2)	487(95)	376(40)	2723(251)	-257(102)	1107(250)	-366(163)
O(3)	1368(138)	327(40)	2914(272)	-35(122)	2215(317)	77(169)
O(4)	2095(195)	568(57)	3770(353)	582(180)	1114(423)	64(237)
N(1)	473(106)	149(34)	1451(222)	1(99)	908(250)	-278(142)
N(2)	505(113)	221(39)	1711(242)	-108(107)	746(265)	-122(157)
N(3)	507(112)	198(38)	2255(267)	11(107)	999(285)	527(164)
C(1)	452(136)	263(51)	2026(328)	110(136)	682(339)	-47(209)
C(2)	905(162)	231(50)	1968(324)	47(150)	1447(372)	168(213)
C(3)	934(165)	273(53)	2452(359)	-197(161)	1883(397)	115(233)
C(4)	401(134)	259(52)	2162(333)	-3(135)	757(341)	-128(211)
C(5)	485(131)	214(46)	1220(265)	-11(127)	722(300)	-13(180)
C(6)	647(140)	129(41)	1320(267)	66(124)	446(309)	310(170)
C(7)	257(126)	252(49)	2295(327)	-114(128)	165(322)	89(207)

TABLE V--Continued

Atom	Anisotropic Temperature Factors X 10^5					
	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
C(8)	475(142)	279(55)	2634(373)	-274(145)	288(368)	-282(232)
C(9)	1012(181)	204(52)	2742(388)	402(157)	1034(424)	457(228)
C(10)	910(171)	242(53)	2796(387)	-292(152)	1447(417)	-1148(234)
C(11)	607(146)	275(53)	1691(310)	194(144)	313(336)	115(208)
C(12)	611(153)	193(48)	3731(444)	-12(138)	2001(427)	-397(235)
H(1)	726	219	1334	. . .	473	. . .
H(2)	726	219	1334	. . .	473	. . .
H(3)	726	219	1334	. . .	473	. . .
H(4)	726	219	1334	. . .	473	. . .
H(7)	726	219	1334	. . .	473	. . .
H(8)	726	219	1334	. . .	473	. . .
H(9)	726	219	1334	. . .	473	. . .
H(10)	726	219	1334	. . .	473	. . .
H(11)	726	219	1334	. . .	473	. . .
H(11)	726	219	1334	. . .	473	. . .
H(N)	726	219	1334	. . .	473	. . .
H(N)	726	219	1334	. . .	473	. . .

TABLE VI

FINAL OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BPGC

L	FO	FC
H=	J, K=	0
2	153	-113
-4	219	-135
-6	278	251
-8	60	-56
H=	0, K=	1
1	740	-755
2	882	856
3	682	630
-4	453	412
-5	403	-356
-6	191	164
-7	167	-181
-8	61	-46
H=	0, K=	2
0	1060	1096
1	1037	-1148
2	1383	-1560
3	294	-280
-4	421	-380
-5	131	-92
-6	137	142
-7	231	216
-8	26	26
H=	0, K=	3
1	359	328
2	1651	2057
3	358	322
-4	551	510
-5	109	89
-6	19	21
-7	99	74
H=	0, K=	4
0	635	-580
1	763	-723
2	954	-934
3	771	759
-4	633	581
-5	492	-478
-6	167	-171
-7	129	127
H=	0, K=	5
1	370	348
2	603	554
3	612	-543
-4	287	226
-5	89	92
-6	14	-46
-7	20	-26
H=	0, K=	6
0	359	-285
1	243	-234
2	471	445
3	309	240
-4	618	521
-5	90	79
-6	361	-358
-7	25	29
H=	0, K=	7
1	168	145
2	775	-718
3	367	-371
-4	200	118
-5	380	342
-6	38	57
-7	69	80
H=	0, K=	8
0	268	261
1	95	35
2	383	-345
3	84	-63
-4	134	121
-5	536	501
-6	112	-112
-7	176	-177
H=	0, K=	9
1	705	-635
2	267	-280
3	94	-73
-4	449	-414
-5	9	1
-6	0	-4
-7	21	31
H=	0, K=	10
0	818	743
1	212	255
2	180	-192
3	197	196
-4	93	-101
-5	155	169
-6	148	178
H=	0, K=	11
1	187	155
2	232	205
3	651	648
-4	89	-107
-5	242	-245
-6	116	-106
H=	0, K=	12
0	546	524
1	492	-437
2	321	-294
3	55	93
-4	119	-125
-5	102	85
-6	151	166
H=	0, K=	13
1	120	-142
2	170	172
3	358	373
-4	444	472
-5	55	-61
-6	19	23
H=	0, K=	14
0	228	-214
1	528	-527
2	47	-44
3	187	172
-4	64	-60
-5	222	-228
H=	0, K=	15
1	200	-208
2	404	393
3	256	-257
-4	198	181
-5	107	112
H=	0, K=	16
0	245	-275
1	271	-291
2	308	299
3	136	143
-4	37	37
H=	0, K=	17
1	280	289
2	59	64
3	230	-249
-4	26	-15
H=	0, K=	18
0	372	-354
1	37	49
2	214	228
3	137	-124
H=	0, K=	19
1	52	67
2	253	-291
H=	1, K=	0
0	812	870
2	64	-114
4	510	-487
6	169	182
-2	433	-361
-4	572	518
-6	270	277
-8	258	-269
H=	1, K=	1
0	705	-636
1	958	-1120
2	313	-369
3	613	614
4	239	-269
5	275	-298
6	146	-173
7	89	-107
-1	634	633
-2	212	213
-3	698	638
-4	588	602
-5	166	-352
-6	139	-126
-7	24	-34
-8	24	-8
H=	1, K=	2
0	325	266
1	224	-158
2	190	-176
3	531	-493
4	62	-73
5	99	139
6	211	297
7	127	-144
-1	1056	1113
-2	357	384
-3	337	-305
-4	152	-130
-5	85	43
-6	243	239
-7	308	238
-8	61	-80
H=	1, K=	3
0	713	-647
1	798	-738
2	984	1087
3	376	321
4	309	-305
5	33	-12
6	115	-131
7	159	138
-1	743	-733
-2	637	646
-3	330	-332
-4	599	555
-5	62	64
-6	400	-376
-7	44	34
-8	37	-53
H=	1, K=	4
0	413	-378
1	83	-71
2	1045	-1043
3	162	-122
4	130	187
5	379	375
6	91	-103
7	47	-52
-1	1013	1035
-2	479	434
-3	889	-816
-4	874	-803
-5	379	-333
-6	230	-239
-7	96	92
-8	105	116
H=	1, K=	5
0	485	474
1	1201	1259
2	783	729
3	325	261
4	96	-63
5	233	-198
6	46	-44
7	163	167
-1	519	500
-2	487	-476
-3	19	-53
-4	298	-231
-5	589	576
-6	116	-131
-7	102	-117
H=	1, K=	6
0	74	32
1	342	-322
2	31	-47
3	55	-36
4	568	533
5	24	-39
6	295	-279
7	71	66
-1	134	231
-2	1446	1334
-3	257	241
-4	593	-533
-5	20	-5
-6	133	-135
-7	20	33
H=	1, K=	7
0	359	306
1	570	563
2	379	-367
3	356	-341
4	520	-431
5	406	-376
6	59	64
7	137	149
-1	581	-570
-2	173	-147
-3	710	-610
-4	318	-340
-5	231	226
-6	541	538
-7	137	-159
H=	1, K=	8
0	383	-348
1	341	-307
2	163	75
3	488	415
4	456	417
5	359	-383
6	39	27
7	35	36
-1	589	-526
-2	66	-46
-3	503	479
-4	47	39
-5	42	53
-6	128	127
-7	100	-91
H=	1, K=	9
0	526	489
1	241	-256
2	417	-430
3	152	152
4	140	122
5	97	-109
6	258	260
-1	255	-227
-2	177	-136
-3	293	-226
-4	583	-528
-5	70	-48
-6	319	320
-7	78	96
H=	1, K=	10
0	117	-62
1	157	179
2	11	35
3	742	803
4	287	-296
5	155	-171
6	20	5
-1	519	-506
-2	469	-426
-3	205	181
-4	152	166
-5	95	-142
-6	82	89
-7	105	-141
H=	1, K=	11
0	29	-13
1	367	-361
2	58	50
3	389	384
4	21	-14
5	40	46
6	148	128
-1	495	459
-2	164	186
-3	333	472
-4	222	-209
-5	198	-218
-6	20	19
H=	1, K=	12
0	496	508
1	396	-368
2	164	159
3	28	-23
4	364	-362
5	30	-53
6	7	2
-1	108	124
-2	233	-219
-3	70	-89
-4	232	268
-5	116	118
-6	92	92
H=	1, K=	13
0	230	-250
1	516	-508
2	207	236
3	177	192
4	223	-212
5	91	90
-1	53	93
-2	224	199
-3	239	223
-4	276	285
-5	150	-160
-6	45	-80
H=	1, K=	14
0	187	-173
1	216	-212
2	0	28

TABLE VI--Continued

L	FO	FC
3	287	-325
4	56	63
5	84	75
-1	544	560
-2	260	-263
-3	252	-246
-4	94	-115
-5	14	38
H=	1, K=	15
0	311	-329
1	72	77
2	466	461
3	151	-121
4	26	-15
5	0	16
-1	265	-293
-2	52	-64
-3	98	-114
-4	70	89
-5	42	67
H=	1, K=	16
0	117	-142
1	36	60
2	29	-21
3	93	95
4	162	141
-1	389	414
-2	248	269
-3	232	-261
-4	102	-120
H=	1, K=	17
0	125	-138
1	565	591
2	29	-14
3	91	-84
-1	45	-42
-2	0	14
-3	119	-124
-4	73	65
H=	1, K=	18
0	96	-90
1	165	-193
2	39	-32
3	28	27
-1	94	-127
-2	332	363
-3	161	197
H=	1, K=	19
0	74	89
1	161	156
2	212	-222
-1	169	-177
-2	74	86
H=	2, K=	0
0	331	361
2	738	727
4	254	-259
6	74	-36
-2	594	613
-4	1164	1129
-6	126	-123
-8	104	-107

L	FO	FC
H=	2, K=	1
0	359	-319
1	413	-393
2	506	-517
3	42	-70
4	78	-58
5	192	182
6	152	-185
7	176	-197
-1	160	-128
-2	368	303
-3	30	-5
-4	396	359
-5	359	-347
-6	70	-87
-7	260	262
-8	122	161
H=	2, K=	2
0	639	-596
1	497	-464
2	209	-186
3	846	-836
4	88	76
5	168	193
6	7	15
7	90	98
-1	160	95
-2	569	-593
-3	198	-229
-4	139	78
-5	545	504
-6	78	-97
-7	177	162
-8	24	-27
H=	2, K=	3
0	834	-823
1	498	491
2	296	311
3	51	-64
4	203	176
5	166	167
6	195	-214
7	149	169
-1	450	-459
-2	673	669
-3	54	50
-4	25	-4
-5	71	-50
-6	430	-396
-7	88	102
-8	124	166
H=	2, K=	4
0	54	-100
1	504	533
2	476	-480
3	264	-271
4	294	322
5	215	197
6	40	-5
7	52	63
-1	353	339
-2	121	129
-3	466	-453
-4	531	-498
-5	50	64
-6	26	-6
-7	55	-79

L	FO	FC
H=	2, K=	5
0	373	389
1	1080	1041
2	261	245
3	356	-317
4	229	237
5	443	-443
6	10	-19
7	115	135
-1	136	-130
-2	23	-71
-3	508	452
-4	309	292
-5	276	274
-6	246	-245
-7	203	-199
-8	89	97
H=	2, K=	6
0	465	437
1	9	-14
2	793	-750
3	89	105
4	401	398
5	137	-181
6	120	-125
7	42	36
-1	318	-279
-2	1198	1166
-3	115	141
-4	263	-249
-5	170	-137
-6	95	84
-7	21	6
H=	2, K=	7
0	273	249
1	650	630
2	567	-516
3	88	-57
4	428	-406
5	285	-273
6	206	215
7	95	98
-1	689	-667
-2	587	-522
-3	155	166
-4	82	72
-5	128	124
-6	181	174
-7	166	-164
H=	2, K=	8
0	306	-299
1	236	-249
2	157	-160
3	524	506
4	229	230
5	224	-242
6	133	109
-1	298	-257
-2	185	225
-3	775	711
-4	130	-118
-5	235	-219
-6	40	-17
-7	98	102
H=	2, K=	9
0	1233	1170

L	FO	FC
1	388	-382
2	319	-306
3	91	137
4	264	-264
5	123	142
6	255	264
-1	332	-324
-2	608	-568
-3	406	-388
-4	235	-219
-5	92	-108
-6	31	-15
-7	66	42
H=	2, K=	10
0	140	-134
1	93	-119
2	360	365
3	536	531
4	265	-262
5	34	-7
6	35	-19
-1	117	-98
-2	405	-387
-3	387	353
-4	225	214
-5	518	-493
-6	43	-69
-7	76	-109
H=	2, K=	11
0	486	460
1	187	-186
2	100	78
3	26	-67
4	72	-64
5	158	138
6	143	146
-1	856	824
-2	18	-14
-3	22	36
-4	87	-72
-5	64	-48
-6	48	-39
H=	2, K=	12
0	46	-6
1	124	-151
2	637	599
3	314	-321
4	262	-277
5	74	-33
-1	85	-62
-2	436	-415
-3	138	121
-4	385	350
-5	86	92
-6	17	-7
H=	2, K=	13
0	467	-469
1	218	-215
2	49	-34
3	82	-95
4	41	-38
5	85	81
-1	447	472
-2	88	94
-3	335	-325
-4	313	306
-5	120	-140

L	FO	FC
H=	2, K=	14
0	187	-169
1	271	261
2	195	195
3	317	-333
4	18	-12
5	47	53
-1	85	-76
-2	325	-309
-3	259	-256
-4	26	-5
-5	198	228
H=	2, K=	15
0	405	-423
1	66	85
2	265	263
3	14	-19
4	130	118
-1	115	-121
-2	195	194
-3	193	-179
-4	160	175
-5	64	-58
H=	2, K=	16
0	0	47
1	423	477
2	109	-111
3	13	-1
4	61	80
-1	23	7
-2	301	320
-3	202	-223
-4	112	-141
H=	2, K=	17
0	159	-178
1	186	206
2	38	56
3	0	-7
-1	69	-95
-2	26	-38
-3	153	167
-4	93	90
H=	2, K=	18
0	71	81
1	23	-42
2	186	-207
-1	141	-138
-2	316	371
-3	104	124
H=	2, K=	19
0	67	93
1	62	102
-1	132	-186
-2	102	-112
H=	3, K=	0
0	655	-664
2	577	586
4	221	-217
6	322	-341
-2	953	940
-4	1198	1151
-6	389	-383

L	FO	FC
-8	11	55
H=	3, K=	1
0	351	-366
1	201	-178
2	408	-420
3	433	-455
4	132	140
5	220	255
6	29	-56
7	26	-10
-1	917	902
-2	40	16
-3	492	-479
-4	243	-227
-5	281	-240
-6	57	-32
-7	279	270
-8	174	180
H=	3, K=	2
0	495	-452
1	272	243
2	289	232
3	615	-635
4	277	263
5	125	-124
6	74	-75
7	216	236
-1	657	-641
-2	609	-624
-3	702	-676
-4	392	374
-5	742	711
-6	358	-368
-7	29	13
-8	34	30
H=	3, K=	3
0	135	-154
1	119	115
2	353	-337
3	217	194
4	447	425
5	31	16
6	172	-167
7	112	124
-1	329	-336
-2	1001	977
-3	82	69
-4	547	-499
-5	182	-158
-6	194	-165
-7	83	91
-8	201	217
H=	3, K=	4
0	185	-178
1	998	986
2	138	-123
3	20	-31
4	101	104
5	53	-65
6	100	108
7	119	130
-1	127	100
-2	601	-549
-3	677	-610
-4	216	-199
-5	318	308
-6	114	117

TABLE VI--Continued

L	FO	FC
-7	261	-288
-8	16	-10
H=	3, K=	5
0	71	98
1	91	83
2	185	-124
3	303	316
4	297	324
5	484	-499
6	79	61
7	24	25
-1	748	-687
-2	471	453
-3	980	918
-4	28	-50
-5	130	136
-6	276	-264
-7	102	-90
-8	65	63
H=	3, K=	6
0	1092	1041
1	567	-537
2	615	-609
3	150	169
4	19	-13
5	82	-102
6	95	86
-1	276	253
-2	235	194
-3	37	16
-4	45	-4
-5	89	90
-6	356	363
-7	90	-104
H=	3, K=	7
0	69	-53
1	24	-30
2	325	-278
3	302	299
4	277	-295
5	253	-249
6	167	192
-1	711	-656
-2	378	-356
-3	488	459
-4	397	379
-5	59	-95
-6	142	129
-7	28	-21
H=	3, K=	8
0	3	28
1	1069	-1016
2	100	-90
3	383	350
4	59	-40
5	117	132
6	143	132
-1	498	437
-2	141	-113
-3	383	350
-4	355	-347
-5	102	-130
-6	66	64
-7	17	-6

L	FO	FC
H=	3, K=	9
0	600	555
1	68	-89
2	169	147
3	27	41
4	442	-430
5	261	290
6	97	93
-1	159	186
-2	816	-782
-3	365	-364
-4	190	191
-5	339	-348
-6	86	-64
-7	27	35
H=	3, K=	10
0	266	-287
1	363	-350
2	435	433
3	432	358
4	114	-105
5	129	139
6	95	-103
-1	704	694
-2	96	-101
-3	117	82
-4	230	233
-5	102	-94
-6	110	-122
-7	91	-59
H=	3, K=	11
0	372	371
1	47	-40
2	191	193
3	543	-545
4	36	31
5	185	188
-1	915	884
-2	76	-109
-3	124	-99
-4	156	156
-5	81	-81
-6	22	-2
H=	3, K=	12
0	471	-463
1	134	-125
2	577	567
3	224	-252
4	203	-196
5	14	-24
-1	191	-196
-2	52	48
-3	457	-481
-4	306	310
-5	149	144
-6	169	-183
H=	3, K=	13
0	400	-396
1	0	-8
2	286	-306
3	238	-245
4	200	227
5	195	205
-1	391	384
-2	207	227

L	FO	FC
-3	202	-188
-4	138	132
-5	0	7
-6	42	56
H=	3, K=	14
0	131	-143
1	388	381
2	169	162
3	190	-218
4	47	52
-1	0	-24
-2	76	-56
-3	375	-357
-4	81	-67
-5	325	353
H=	3, K=	15
0	187	-190
1	61	-56
2	93	-85
3	21	7
4	286	319
-1	279	-324
-2	188	186
-3	69	-95
-4	204	-231
-5	91	-121
H=	3, K=	16
0	175	192
1	375	403
2	215	-264
3	25	-20
-1	119	125
-2	227	239
-3	158	-142
-4	102	-121
H=	3, K=	17
0	100	125
1	104	126
2	32	-37
3	113	130
-1	83	-76
-2	36	-1
-3	328	368
-4	0	8
H=	3, K=	18
0	82	122
1	162	-185
2	209	-244
-1	17	23
-2	31	41
-3	60	-61
H=	3, K=	19
0	131	151
-1	166	-165
H=	4, K=	0
0	448	-462
2	282	277
4	237	285
6	330	-330
-2	291	295

L	FO	FC
-4	387	366
-6	157	-179
-8	118	130
H=	4, K=	1
0	776	-758
1	867	841
2	661	-660
3	738	-745
4	52	67
5	6	-11
6	62	64
-1	249	227
-2	211	-170
-3	448	-426
-4	295	-284
-5	553	541
-6	157	178
-7	38	42
-8	107	112
H=	4, K=	2
0	56	-12
1	635	580
2	46	-28
3	335	327
4	222	230
5	268	-284
6	101	-109
-1	1023	-987
-2	465	-439
-3	337	316
-4	310	275
-5	401	383
-6	194	-198
-7	241	-266
-8	69	65
H=	4, K=	3
0	195	208
1	165	147
2	681	-660
3	316	323
4	480	464
5	177	198
6	68	79
-1	594	-545
-2	477	447
-3	329	-293
-4	552	-528
-5	331	-332
-6	112	110
-7	41	-53
-8	58	61
H=	4, K=	4
0	614	583
1	466	439
2	173	-144
3	316	284
4	114	-114
5	325	-319
6	183	192
-1	925	-866
-2	620	-581
-3	314	283
-4	47	21
-5	174	179
-6	98	94

L	FO	FC
-7	399	-395
-8	160	-169
H=	4, K=	5
0	660	615
1	760	-734
2	38	22
3	321	318
4	156	178
5	72	-79
6	27	21
-1	199	-174
-2	854	824
-3	1078	1048
-4	111	-141
-5	275	-280
-6	81	-56
-7	47	49
H=	4, K=	6
0	1198	1132
1	462	-442
2	399	-389
3	114	88
4	419	-418
5	107	109
6	140	140
-1	25	34
-2	909	-868
-3	47	-87
-4	226	219
-5	110	91
-6	352	397
-7	100	126
H=	4, K=	7
0	689	-622
1	626	-566
2	105	-92
3	236	241
4	205	-223
5	35	26
6	34	-32
-1	22	-33
-2	610	-602
-3	723	677
-4	271	267
-5	392	-382
-6	109	-92
-7	105	-122
H=	4, K=	8
0	646	539
1	546	-528
2	158	137
3	171	-166
4	0	-2
5	182	196
6	119	134
-1	755	731
-2	578	-551
-3	152	-164
-4	254	-212
-5	176	-157
-6	110	110
-7	350	394
H=	4, K=	9

L	FO	FC
0	309	-292
1	84	112
2	721	672
3	54	-50
4	170	-162
5	136	128
-1	13	-7
-2	420	-408
-3	182	-193
-4	672	648
-5	116	-87
-6	105	-81
-7	97	-104
H=	4, K=	10
0	222	-223
1	95	-95
2	152	-135
3	0	49
4	47	61
5	59	73
-1	785	752
-2	156	148
-3	212	-219
-4	90	93
-5	308	-309
-6	249	-280
-7	77	68
H=	4, K=	11
0	5	14
1	372	362
2	244	232
3	302	-293
4	41	-65
5	29	29
-1	288	264
-2	200	-172
-3	166	-160
-4	202	193
-5	350	377
-6	9	-12
H=	4, K=	12
0	423	-420
1	54	-63
2	92	-86
3	56	72
4	70	72
5	0	-9
-1	226	-246
-2	566	566
-3	0	11
-4	298	334
-5	53	90
-6	171	-189
H=	4, K=	13
0	67	92
1	51	20
2	227	-236
3	188	-194
4	67	101
-1	25	-42
-2	152	181
-3	254	-226
-4	288	-308
-5	98	98
-6	82	95

TABLE VI--Continued

L	FO	FC
H=	4, K=	14
0	8	0
1	24	-35
2	160	196
3	21	29
4	185	218
-1	416	-444
-2	174	-183
-3	25	-30
-4	56	-90
-5	59	81
H=	4, K=	15
0	244	230
1	187	-202
2	191	-218
3	128	159
-1	0	-21
-2	299	319
-3	664	647
-4	193	-165
-5	23	-39
-6	75	54
-7	199	-202
H=	5, K=	5
0	488	447
1	815	-799
2	69	27
3	100	130
4	10	34
5	40	12
6	45	48
-1	426	394
-2	198	-167
-3	337	324
-4	76	-106
-5	369	-368
-6	168	167
-7	229	242
H=	5, K=	6
0	426	389
1	197	-168
2	80	42
3	51	-37
4	292	-272
5	175	-184
-1	25	23
-2	535	-522
-3	433	-427
-4	535	503
-5	106	97
-6	233	262
-7	0	29
H=	5, K=	7
0	354	-345
1	505	-496
2	165	150
3	301	318
4	159	156
5	42	-33
-1	275	251
-2	420	-399
-3	167	169
-4	282	276
-5	277	-268
-6	129	-148
-7	133	124
H=	5, K=	8
0	55	32
1	134	-119
2	47	12
3	117	-93
4	46	13
5	131	136
-1	331	321
-2	359	-374
-3	704	-714
-4	34	-14
-5	227	209
-6	77	90
-7	241	267
H=	5, K=	9
0	566	-550
1	182	204
2	171	160
3	368	383
4	120	-130
5	84	94
-1	232	-217
-2	47	58
-3	12	-22
-4	287	307
-5	11	12
-6	447	-506
-7	194	-231
H=	5, K=	10
0	77	-71
1	64	32
2	241	-245
3	62	73
4	77	89
5	119	118
-1	693	689
-2	323	321
-3	194	-173
-4	255	-288
-5	137	115
-6	63	78
H=	5, K=	11
0	149	136
1	31	-28
2	149	176
3	189	-209
4	45	62
-1	344	-343
-2	114	136
-3	149	126
-4	351	378
-5	531	594
-6	82	-95
H=	5, K=	12
0	44	-24
1	434	-453
2	274	-262
3	0	-28
4	134	166
-1	131	-154
-2	548	574
-3	57	-34
-4	282	-325
-5	205	-232
-6	27	14
H=	5, K=	13
0	137	144
1	175	176
2	160	-157
3	43	-27
4	70	42
-1	141	-131
-2	318	-338
-3	89	-117
-4	97	-106
-5	204	220
H=	5, K=	14
0	48	-51
1	100	-93
2	18	1
3	212	261
-1	19	-10
-2	103	126
-3	354	380
-4	157	-158
-5	78	-75
H=	5, K=	15
0	408	417
1	9	-11
2	185	-202
-1	123	119
-2	155	-151
-3	188	-206
-4	195	-228
H=	5, K=	16
0	0	17
1	7	-15
2	80	105
-1	0	-7
-2	109	-128
-3	208	219
-4	189	239
H=	5, K=	17
0	135	161
1	261	-315
-1	171	187
-2	49	80
-3	94	128
H=	6, K=	0
0	119	-104
2	790	-813
4	249	224
-2	416	407
-4	491	-483
-6	163	150
H=	6, K=	1
0	34	-24
1	215	234
2	191	-193
3	76	54
4	101	-118
5	230	-226
-1	744	-699
-2	501	-507
-3	516	518
-4	291	-288
-5	199	206
-6	152	141
-7	114	-126
H=	6, K=	2
0	25	20
1	272	-429
2	180	-178
3	337	349
4	141	155
5	34	12
-1	25	38
-2	392	388
-3	414	427
-4	344	-347
-5	370	-380
-6	10	-6
-7	102	121
H=	6, K=	3
0	555	536
1	286	276
2	279	-264
3	152	123
4	319	-331
5	26	3
-1	33	26
-2	518	-523
-3	178	-174
-4	12	-18
-5	277	-265
-6	243	246
-7	90	-100
H=	6, K=	4
0	142	152
1	276	-281
2	297	301
3	227	218
4	59	-83
5	165	-191
-1	189	149
-2	65	-58
-3	533	527
-4	243	247
-5	319	-328
-6	86	-99
-7	0	6
H=	6, K=	5
0	480	449
1	356	-320
2	141	155
3	275	-283
4	150	-157
5	42	55
-1	383	359
-2	305	247
-3	186	-197
-4	171	204
-5	83	-78
-6	140	140
-7	282	317
H=	6, K=	6
0	279	-282
1	18	46
2	271	257
3	42	-37
4	371	-384
5	26	-19
-1	248	-244
-2	91	-95
-3	203	-201
-4	477	493
-5	11	10
-6	64	-55
-7	44	21
H=	6, K=	7
0	542	-514
1	148	-142
2	142	148
3	73	-46
4	67	68
5	111	125
-1	391	393
-2	97	-92
-3	97	-95
-4	175	-163
-5	83	-98
-6	218	-217
-7	193	220
H=	6, K=	8
0	0	-36
1	381	403
2	211	221
3	219	-217
4	38	45
-1	18	-36
-2	86	-81
-3	410	-433
-4	94	-83
-5	265	272
-6	191	-210
-7	59	22
H=	6, K=	9
0	391	-368
1	278	281
2	251	237
3	101	115
4	101	122
-1	193	-181
-2	450	441
-3	68	75
-4	64	-63
-5	69	-104
-6	190	-224
H=	6, K=	10
0	43	-52
1	391	394
2	189	-210
3	204	-221
4	176	209
-1	195	209
-2	228	219
-3	133	-138
-4	256	-283
-5	167	184
-6	134	150
H=	6, K=	11
0	88	-109
1	228	234
2	22	-16
3	44	61
4	22	-21
-1	587	-594
-2	152	173
-3	197	211
-4	57	61
-5	236	263
-6	55	-67
H=	6, K=	12
0	0	19
1	56	-53
2	450	-470
3	177	191
-1	153	-151
-2	215	232
-3	5	9
-4	233	-256
-5	138	-153
H=	6, K=	13
0	86	106
1	209	199
2	70	-78
3	177	177
-1	457	-497
-2	243	-275
-3	80	65
-4	0	22
-5	154	188
H=	6, K=	14
0	152	203
1	370	-410
2	64	84
-1	244	-277
-2	151	167
-3	279	303
-4	172	-198
H=	6, K=	15
0	352	374
1	27	-40
2	17	63
-1	0	18
-2	144	-170
-3	50	-83
-4	48	45
H=	6, K=	16
0	98	-134
1	139	-134
-1	113	143
-2	80	-79
-3	472	538

TABLE VI--Continued

L	FO	FC
H=	7, K=	0
0	540	488
2	520	-557
4	120	-127
-2	314	-297
-4	495	-487
-6	395	404
H=	7, K=	1
0	130	-128
1	69	-81
2	85	116
3	175	185
4	78	-99
5	87	-57
-1	433	-396
-2	873	-859
-3	694	688
-4	51	-52
-5	201	-204
-6	29	11
-7	0	-6
H=	7, K=	2
0	280	265
1	365	-358
2	51	-21
3	179	165
4	34	28
5	215	233
-1	389	384
-2	68	43
-3	50	-44
-4	313	-276
-5	404	-405
-6	119	97
-7	195	220
H=	7, K=	3
0	247	248
1	273	251
2	338	315
3	7	-11
4	259	-262
-1	44	38
-2	862	-854
-3	35	-30
-4	480	461
-5	261	-265
-6	87	85
-7	50	-69
H=	7, K=	4
0	214	-194
1	394	-393
2	252	260
3	13	-31
4	115	140
-1	473	473
-2	211	195
-3	160	143
-4	466	469
-5	280	-276
-6	127	-149
-7	189	189
H=	7, K=	5
0	314	281
1	27	-34
2	22	-13
3	477	-511
4	51	-67
-1	145	130
-2	111	-96
-3	435	-424
-4	397	419
-5	108	133
-6	41	-48
-7	211	237
H=	7, K=	6
0	893	-905
1	94	86
2	195	180
3	103	-108
4	49	49
-1	124	-99
-2	187	173
-3	97	-100
-4	429	443
-5	44	-38
-6	178	-198
-7	54	22
H=	7, K=	7
0	68	-33
1	98	106
2	268	-286
3	337	-321
4	285	325
-1	285	306
-2	187	195
-3	313	-306
-4	180	-178
-5	153	154
-6	242	-234
H=	7, K=	8
0	61	-61
1	410	420
2	101	92
3	192	-196
4	65	59
-1	326	-314
-2	87	80
-3	206	-210
-4	0	-35
-5	208	222
-6	237	-252
H=	7, K=	9
0	50	71
1	264	272
2	464	-465
3	154	169
-1	41	72
-2	406	384
-3	23	37
-4	139	-147
-5	83	-109
-6	140	-146
H=	7, K=	10
0	297	320
1	451	457
2	174	-198
3	138	-147
-1	73	26
-2	16	-11
-3	135	141
-4	211	-229
-5	279	331
-6	103	120
H=	7, K=	11
0	190	215
1	79	-103
2	159	-171
3	147	166
-1	393	-406
-2	19	-10
-3	217	214
-4	44	46
-5	0	-26
H=	7, K=	12
0	337	335
1	118	-155
2	223	-233
-1	96	-89
-2	111	-136
-3	128	-147
-4	108	-116
-5	71	-82
H=	7, K=	13
0	180	193
1	32	18
2	67	93
-1	152	-152
-2	456	-506
-3	106	107
-4	130	167
H=	7, K=	14
0	117	114
1	258	-275
-1	75	117
-2	43	-72
-3	20	9
H=	7, K=	15
0	63	125
-1	158	207
-2	296	-333
H=	8, K=	0
0	197	177
2	158	-198
4	211	-218
-2	1243	-1246
-4	309	312
-6	249	286
H=	8, K=	1
0	215	-204
1	399	-359
2	189	174
3	97	131
4	44	17
-1	72	72
-2	201	-179
-3	704	719
-4	238	249
-5	392	-399
-6	213	-237
-7	96	107
H=	8, K=	2
0	503	495
1	42	-20
2	107	106
3	24	12
4	42	-37
-1	584	552
-2	375	-346
-3	570	-563
-4	273	300
-5	300	-298
-6	79	46
-7	170	193
H=	8, K=	3
0	538	-472
1	67	39
2	279	290
3	18	16
4	142	-134
-1	155	-190
-2	192	-209
-3	99	96
-4	532	523
-5	206	-202
-6	317	-365
H=	8, K=	4
0	45	50
1	206	-226
2	0	-2
3	191	-193
4	105	120
-1	882	853
-2	244	247
-3	131	-106
-4	121	127
-5	38	4
-6	233	-263
H=	8, K=	5
0	49	43
1	335	309
2	176	185
3	168	-187
-1	320	-335
-2	16	28
-3	339	-328
-4	325	331
-5	276	292
-6	91	-79
H=	8, K=	6
0	535	-514
1	318	-338
2	190	-184
3	28	-39
-1	32	10
-2	191	153
-3	117	-114
-4	22	-11
-5	101	-104
-6	164	-190
H=	8, K=	7
0	163	180
1	404	402
2	87	-102
3	276	-245
-1	46	-29
-2	0	6
-3	285	-276
-4	297	-331
-5	182	195
-6	52	89
H=	8, K=	8
0	32	2
1	33	-45
2	119	98
3	263	272
-1	300	-290
-2	24	-27
-3	110	134
-4	33	27
-5	93	117
-6	148	-150
H=	8, K=	9
0	94	116
1	100	118
2	427	-440
-1	233	258
-2	124	124
-3	97	117
-4	173	-176
-5	99	-141
H=	8, K=	10
0	211	239
1	33	6
2	31	11
-1	100	-104
-2	228	-261
-3	217	227
-4	90	114
-5	217	255
H=	8, K=	11
0	0	-7
1	367	-415
2	97	-115
-1	28	-27
-2	104	92
-3	184	229
-4	74	79
H=	8, K=	12
0	189	210
1	103	-105
-1	166	198
-2	201	-218
-3	226	-253
-4	104	122
H=	8, K=	13
0	84	-97
-1	113	88
-2	177	-210
-3	107	135
H=	9, K=	0
0	99	135
2	140	121
-2	571	-581
-4	296	306
-6	128	162
H=	9, K=	1
0	238	-233
1	437	-445
2	133	134
3	161	197
-1	120	84
-2	87	-85
-3	88	-97
-4	52	-127
-5	46	-45
-6	288	-347
H=	9, K=	2
0	221	193
1	63	45
2	54	53
3	124	-188
-1	239	234
-2	356	-340
-3	179	-151
-4	58	35
-5	186	231
-6	54	121
H=	9, K=	3
0	455	-433
1	75	73
2	222	232
3	74	71
-1	255	272
-2	252	248
-3	136	131
-4	220	252
-5	0	5
-6	257	-295
H=	9, K=	4
0	198	204
1	47	-44
2	58	-86
-1	184	180
-2	164	190
-3	163	-162
-4	200	-237
-5	197	221
-6	233	243
H=	9, K=	5
0	274	-256
1	62	74
2	42	11
-1	307	-312
-2	75	79
-3	122	-121
-4	388	400
-5	95	133
-6	20	35
H=	9, K=	6

TABLE VI--Continued

L	FO	FC
H= 9, K= 8		
0	27	-11
1	45	59
2	352	-367
-1	10	-22
-2	229	240
-3	47	-44
-4	396	-428
-5	147	-173
H= 9, K= 7		
0	147	190
1	208	219
2	51	11
-1	162	-175
-2	257	-280
-3	61	69
-4	103	-118
-5	258	302
H= 9, K= 9		
0	360	393
1	56	-81
-1	134	120
-2	212	-223
-3	4	29
-4	101	-141
H= 9, K= 10		
0	91	122
1	120	-145
-1	214	-249
-2	219	226
-3	209	232
-4	112	-118
-5	263	-325
H= 9, K= 11		
0	84	98
1	181	-235
-1	54	-68
-2	149	-177
-3	384	485
-4	219	276
H= 9, K= 11		
0	86	89
-1	146	177
-2	54	-94
-3	76	-83
H= 10, K= 0		
0	367	-399
-2	250	-270
-4	181	-180
H= 10, K= 1		
0	117	-101
1	34	9
-1	161	162
-2	73	105
-3	47	-40
-4	107	-122
-5	197	-196
H= 10, K= 2		
0	94	64
1	339	373
-1	21	-13
-2	207	222
-3	305	-336
-4	51	55
-5	126	135
H= 10, K= 3		
0	301	-313
1	145	164
-1	168	-214
-2	176	183
-3	126	127
-4	96	-114
-5	102	-131
H= 10, K= 4		
0	115	157
1	152	170
-1	89	-115
-2	250	269
-3	110	-106
-4	222	-238
-5	284	340
H= 10, K= 5		
0	24	-4
1	161	201
-1	512	-560
-2	52	43
-3	277	312
-4	65	69
H= 10, K= 6		
0	55	68
-1	112	-148
-2	30	18
-3	52	61
-4	393	-458
H= 10, K= 7		
0	342	367
-1	363	-381
-2	272	-276
-3	791	940
-4	58	82

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CHAPTER IV

DISCUSSION AND CONCLUSION

Thermal Motion

All atoms in a molecule undergo a certain amount of vibration. This vibration increases with increasing temperatures; thus, it is called thermal motion. The thermal motion of an atom results from the superposition of all the normal modes of vibration in the crystal and yields a very complicated result (1). The net effect of vibration is to spread out the electron density of the atom over a finite volume. The spreading of electron density over an atom's equilibrium position results in a volume element consistent with the bonding for the complex involved. Since a vibrating atom possesses a scattering power less than that of a stationary atom, it is necessary to determine the vibrational contributions to the scattering factor through x-ray methods. A first approximation would be to assume that each sphere of vibration possesses a constant radius and is, therefore, isotropic. This would produce an individual temperature parameter for each atom, $B = 8\pi^2\bar{u}^2$, where $\bar{u}^2$ represents the root-mean-square amplitude of atomic vibration. As mentioned in the previous chapter, this produces an approximate model for a tentative structure,

but it represents each atom as a centroid. A more accurate description of the temperature factor is given by considering the thermal motion as anisotropic. The anisotropic model contains all of the information normally obtained on thermal motion. The anisotropic temperature factor is expressed as,

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)],$$

where h, k, and l are the indices of a reflection and the B terms are components of a symmetry second-order tensor, representing the vibrational modes for each atom of the molecule (3; 8, p. 44). The six B terms are convenient to use in least squares refinement.

One can compute the directions of each principal axis and the root-mean-square displacement along each axis of the thermal ellipsoid from a principal axis transformation done on the exponential forms containing the B terms. Table VII gives these root-mean-square displacements for BPGC. Figure 3 shows a CalComp plot of the molecule with fifty percent probability ellipsoids (4, p. 220; 5). From the figure, one can see that the principal axes with the longest root-mean-square amplitude for some atoms are not perpendicular to the plane of the bipyridyl ring. This would indicate that some poor data exist in the reflection list, which resulted in some difficulty in the least squares convergence. These slight abnormalities are not

TABLE VII

ROOT-MEAN-SQUARE AMPLITUDES (Å) OF VIBRATION IN THE PRINCIPAL AXES DIRECTIONS FOR THE ATOMS IN BPGC

Atom	Axis 1	Axis 2	Axis 3
Cu	0.1283	0.1672	0.2310
Cl	0.1821	0.2097	0.2520
O(1)	0.1121	0.1917	0.2735
O(2)	0.1388	0.2411	0.2937
O(3)	0.2155	0.2403	0.3095
O(4)	0.2750	0.3289	0.3660
N(1)	0.1190	0.1590	0.2174
N(2)	0.1504	0.1929	0.2270
N(3)	0.1352	0.1735	0.2702
C(1)	0.1437	0.2159	0.2417
C(2)	0.1747	0.1968	0.2569
C(3)	0.1472	0.2318	0.2807
C(4)	0.1372	0.2090	0.2511
C(5)	0.1406	0.1902	0.1941
C(6)	0.1312	0.1806	0.2102
C(7)	0.1128	0.2109	0.2638
C(8)	0.1352	0.2291	0.2860
C(9)	0.1507	0.2389	0.2921
C(10)	0.1305	0.1969	0.3288
C(11)	0.1308	0.1820	0.3324
C(12)	0.1667	0.2238	0.2268

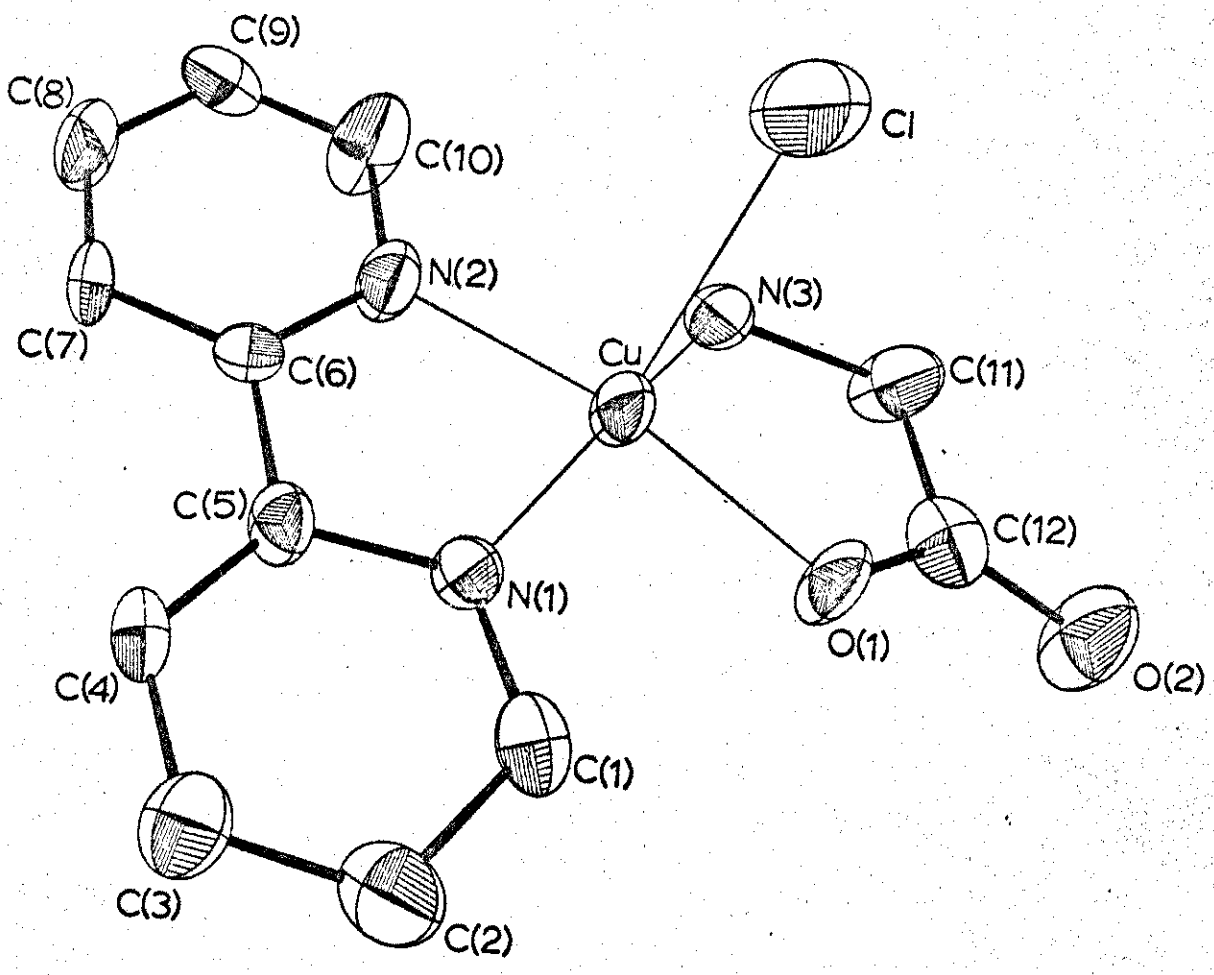

Fig. 3--The fifty percent probability thermal ellipsoids from the thermal parameters of BPGC. View is twisted ten degrees along the Cu-N(1) axis and also the Cu-N(2) axis with copper as the origin.

reflected to any major extent in the bond distances, however.

Molecular and Crystal Structures

Figure 4 shows the entire unit cell and atoms located in the region twenty percent beyond the cell in each direction. The viewing direction is rotated twenty degrees along the c axis and twelve degrees along the a axis. The calculated hydrogen positions are not shown. Bond distances are given in Table VIII. Valance angles for BPCG are given in Table IX.

TABLE VIII

BOND LENGTHS (Å) IN BPGC

Atom 1	Atom 2	Distance Apart (Å)
Cu	O(1)	1.957(8)
Cu	N(3)	2.025(10)
Cu	N(1)	2.010(9)
Cu	N(2)	2.027(10)
Cu	Cl	2.635(4)
O(1)	C(12)	1.298(15)
N(1)	C(1)	1.339(16)
N(1)	C(5)	1.350(14)
N(2)	C(6)	1.342(15)
C(1)	C(2)	1.417(18)
C(2)	C(3)	1.392(18)
C(3)	C(4)	1.426(18)
C(4)	C(5)	1.358(17)
C(5)	C(6)	1.506(16)
C(6)	C(7)	1.394(16)
C(7)	C(8)	1.347(18)
C(8)	C(9)	1.351(18)
C(9)	C(10)	1.374(19)
C(10)	N(2)	1.316(16)
C(11)	N(3)	1.492(16)
C(12)	C(11)	1.533(18)
C(12)	O(2)	1.244(18)

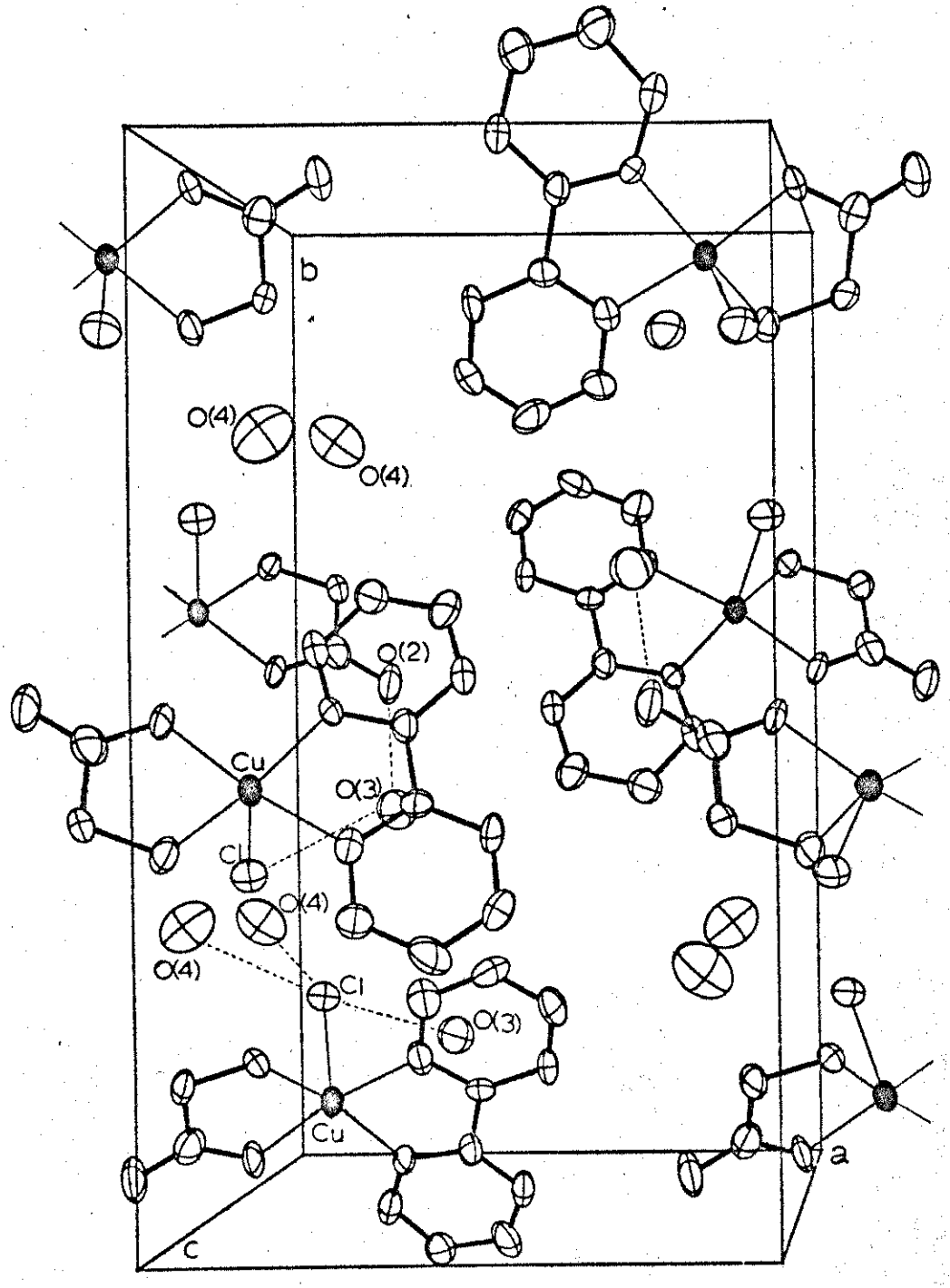

Fig. 4--The unit cell structure of BPGC (See text for further planation.)

TABLE IX

VALENCE ANGLES (DEGREES) IN THE BPGC MOLECULE

Atoms Forming Angle			Angle
Cu	- O(1)	- C(12)	115.5(7)
Cu	- N(1)	- C(1)	125.3(7)
Cu	- N(1)	- C(5)	114.5(7)
CU	- N(2)	- C(6)	113.8(7)
Cu	- N(2)	- C(10)	127.1(8)
Cu	- N(3)	- C(11)	107.5(7)
Cl	- Cu	- O(1)	97.5(6)
Cl	- Cu	- N(1)	100.3(6)
Cl	- Cu	- N(2)	92.7(6)
Cl	- Cu	- N(3)	96.6(6)
O(1)	- Cu	- N(1)	93.0(3)
O(1)	- Cu	- N(3)	86.7(3)
O(1)	- C(12)	- O(2)	123.9(12)
O(1)	- C(12)	- C(11)	116.7(10)
O(2)	- C(12)	- C(11)	119.4(11)
N(1)	- Cu	- N(2)	81.6(3)
N(1)	- C(1)	- C(2)	122.5(10)
N(1)	- C(5)	- C(4)	122.2(10)
N(1)	- C(5)	- C(6)	114.3(9)
N(2)	- Cu	- N(3)	96.7(3)
N(2)	- C(6)	- C(5)	115.4(9)
N(2)	- C(6)	- C(7)	121.1(10)
N(2)	- C(10)	- C(9)	121.6(12)
N(3)	- C(11)	- C(12)	112.7(10)
C(1)	- N(1)	- C(5)	120.1(9)
C(1)	- C(2)	- C(3)	116.4(11)
C(2)	- C(3)	- C(4)	120.5(11)
C(3)	- C(4)	- C(5)	118.4(11)
C(4)	- C(5)	- C(6)	123.6(10)
C(5)	- C(6)	- C(7)	123.6(10)
C(6)	- N(2)	- C(10)	119.0(10)
C(6)	- C(7)	- C(8)	118.8(11)
C(7)	- C(8)	- C(9)	119.6(12)
C(8)	- C(9)	- C(10)	119.8(12)

One can easily see that the coordination about the copper atom is distorted from octahedral. One would predict from Table I that the most probable structure would be distorted octahedral.

From the least squares mean plane calculation, Table X, one can see that the copper atom is slightly above the plane of the four atoms coordinated to it. This could be due to steric interaction of the glycine group and the chlorine atom with the central copper atom.

It has been postulated by Hamilton (2, p. 13) that the O - H...Cl bonding distance is 3.10 Å to 3.20 Å. In the same article, he also postulates the O-H...O bonding distance to be from 2.70 Å to 2.80 Å.

The chlorine atom of BPGC is surrounded by three oxygen atoms which are approximately equidistant to it. From the bond distances found, it is apparent that these bonds are most probably hydrogen bonds. The proposed hydrogen bonded distances are 3.15, 3.20 and 3.19 Å for the two O(4) - H...Cl and O(3) - H...Cl bonds, and are shown in Figure 5. The O(2) and O(3) atoms also indicate, by their distance apart, that they could possess some hydrogen bonding between them. The proposed hydrogen bonded distance for O(2)...H - O(3) is approximately 2.76 Å, and can be seen in Figure 4.

TABLE X

EQUATIONS OF THE LEAST SQUARES BEST PLANES THROUGH THE TWO RING SYSTEMS OF BIPYRIDYL IN THE MOLECULE OF BPGC AND THE DEVIATION OF ATOMS FROM THE BEST PLANES

Ring	Equations of Best Planes
Ring 1*	0.0397X + 0.4478Y - 0.8933Z = -1.3879
Ring 2*	0.1186X + 0.5054Y - 0.8547Z = -1.0212
Ring 1 + Ring 2	0.0789X + 0.4835Y - 0.8717Z = -1.1533

Distances of Atoms from Best Planes (Å)

Atoms	Ring 1	Ring 2	Ring 1 + Ring 2
N(1)	0.2022(89)	-0.0143(89)**	0.0003(89)**
N(2)	-0.0162(94)**	-0.0199(94)	-0.0929(94)**
C(1)	0.3433(125)	0.0112(125)**	0.0742(125)**
C(2)	0.3278(125)	0.0002(125)**	0.0541(125)**
C(3)	0.1865(132)	-0.0082(132)**	-0.0171(132)**
C(4)	0.0781(127)	0.0053(126)**	-0.0545(126)**
C(5)	0.0945(111)	0.0058(111)**	-0.0404(111)**
C(6)	0.0208(117)**	0.0531(111)	-0.0425(111)**
C(7)	-0.0147(124)**	0.1578(124)	-0.0028(124)**
C(8)	0.0040(135)**	0.2762(134)	-0.0755(135)**
C(9)	0.0009(139)**	0.2359(137)	0.0584(137)**
C(10)	0.0051(137)**	0.1006(136)	-0.0929(94)**

*Rings are defined in figure 3.

**Atom used to define the least squares plane.

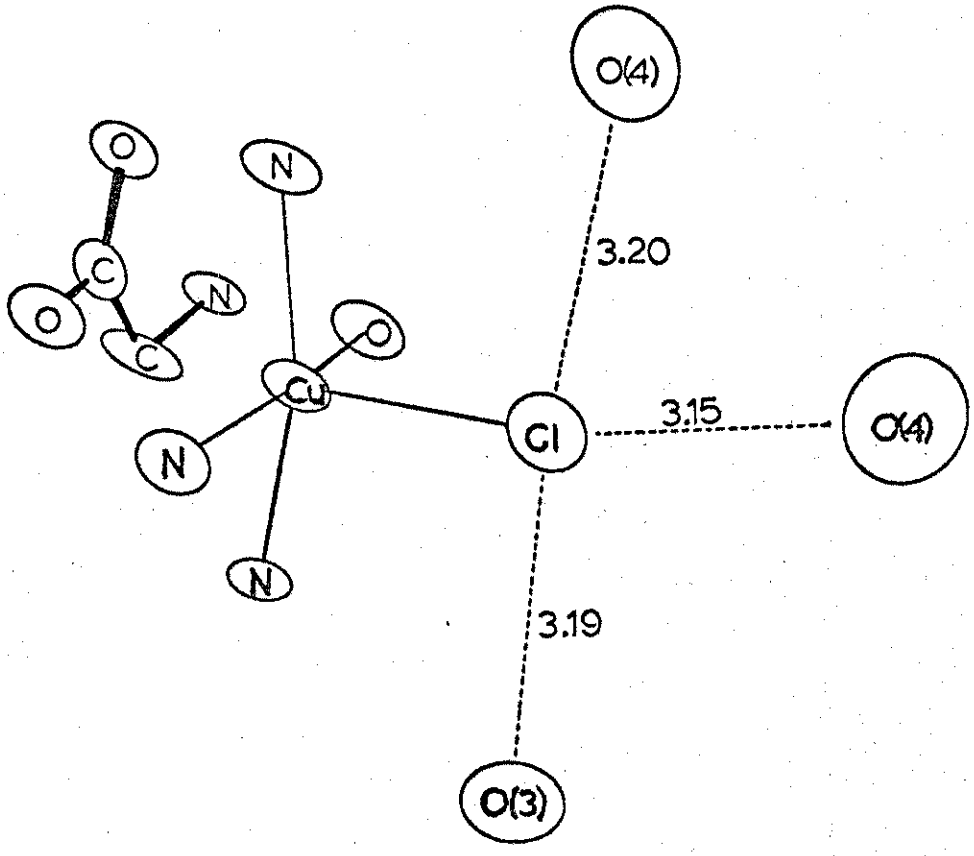

Fig. 5--The hydrogen bonded environment surrounding the chlorine atom, with symmetry related glycine group opposite to the chlorine. (See text for further explanation.)

TABLE XI

EQUATIONS OF THE LEAST SQUARES BEST PLANES THROUGH THE FIVE ATOM CENTRAL COORDINATION AND GLYCINE LIGAND OF BPGC AND THE DEVIATION OF ATOMS FROM THE BEST PLANES

Equations of Best Planes

Plane 1. . . . . $-0.1372X + 0.5794Y - 0.8034Z = -1.4082$

Plane 2. . . . . $-0.1365X + 0.5792Y - 0.0837Z = -1.3615$

Distances of Atoms from Best Planes (Å)

Atoms	Plane 1	Plane 2
Cu	0.2358(15)	0.1886(15)*
N(1)	-0.0641(89)*	-0.1099(89)*
N(2)	0.0610(94)*	0.0146(94)*
N(3)	-0.0594(99)*	-0.1079(99)*
O(1)	-0.0625(81)*	0.0146(81)*
O(2)	-0.1216(89)	-0.1710(89)
C(11)	0.0683(138)	0.0190(138)
C(12)	-0.0146(124)	-0.0343(124)

*Atom used to define the least squares plane.

From Table XI one can see that the least squares best planes through the bipyridyl system indicate that the two bipyridyl rings are not coplanar. The dihedral angle between the planes is approximately six degrees. It is possible to see this puckering of the two rings in Figure 4. This is unusual since other copper structures coordinated to 2,2'-bipyridyl show the pyridine ring as planar (6, 9).

The distance between the C(5) and C(6) atoms indicates a small amount of π bonding, if any, between them, as compared with the other bond distances of other atoms composing the rings. Merritt (7) has shown that the free bipyridyl system is in the least sterically hindered position, with the two nitrogen atoms opposing each other by approximately 180 degrees relative to the center of the molecule. The N(1) - Cu - (N(2) bond angle is only eighty-one degrees. These facts could cause a weakening of the C(5)-C(6) bond by causing a bending stress on the bond.

The glycine ligand could be a stabilizing factor in the tetrahedral distortion due to the sp^3 nature of the C(11) and N(3) atoms. These sp^3 bonds cause a slight misalignment of the sp^2 bonded O(2), C(12), and O(1) atoms. The steric configuration of the molecule is best seen in Figure 6.

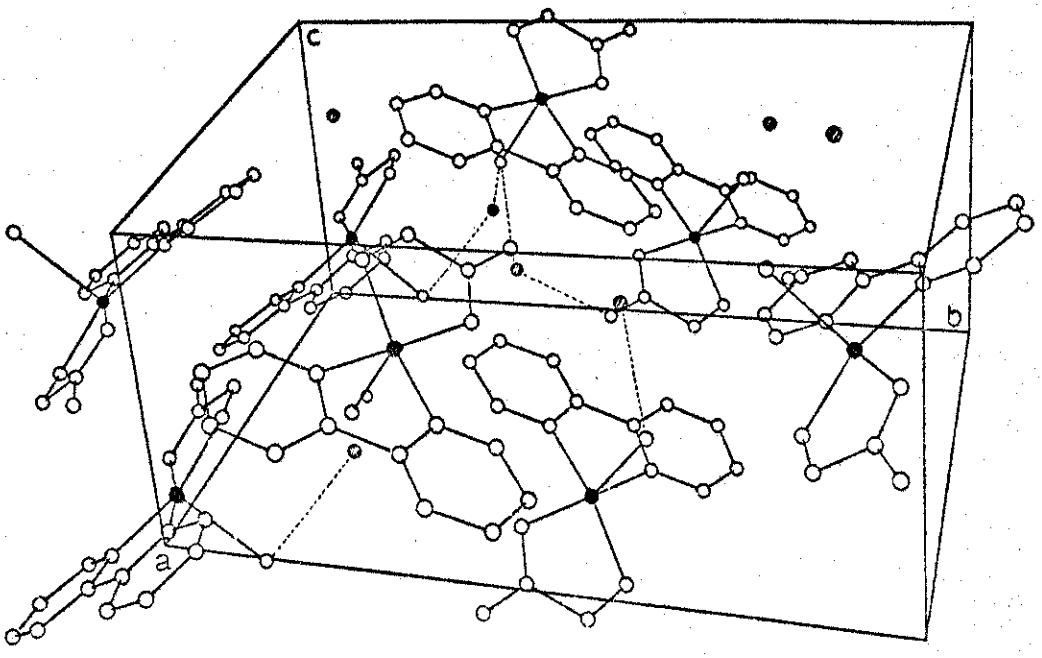

Fig. 6--The unit cell of BPGC. Viewing direction is rotated twenty degrees along the a axis and twelve degrees along the c axis.

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APPENDIX

An IBM 360 computer program was used in the determination of diffractometer linearity. This program produces a series of printer plotted graphs of R index verses $\sin^2\theta$, containing a data point for each reflection. From these graphs, it is possible to observe the contribution of individual reflections as well as small groups of reflections to the overall R index. The input to this program consists of $\sin^2\theta$ and individual R index for each reflection observed.

```
C  ************************************************************
C  *     THIS PROGRAM READS THE SINE SQUARED THETA AND THE    *
C  *  INDIVICUAL RESIDUAL INDEXES FOR A SET OF REFLECTIONS    *
C  *  STORED ON TAPE AND GENERATES A GRAPH OF SINE SQUARED    *
C  *  THETA VERSES THE INDIVIDUAL R VALUES.  THE COLUMNS      *
C  *  ARE THEN INDEPENDANTLY AVERAGED AND THE AVERAGE         *
C  *  SUPERIMPOSED ON THE GRAPH.  THE GRAPH IS INTERPRETED    *
C  *  AS:                                                     *
C  *    A) EACH LETTER CORRESPONDS TO BETWEEN ONE AND         *
C  *       TWENTY SEVEN REFLECTIONS REPRESENTED BY THE       *
C  *       LETTERS FROM A THROUGH Z PLUS *.                  *
C  *    B) EACH OF THE DOTS REPRESENT THE AVERAGE OF ALL      *
C  *       DATA POINTS IN THE COLUMN.                        *
C  *    EACH GRAPH GENERATED IS AN AMPLIFICATION OF THE      *
C  *  PREVIOUS GRAPH.  FROM THESE GRAPHS IT IS POSSIBLE      *
C  *  TO VISUALLY DETERMINE THE CUTOFF POINT FOR THE HIGH    *
C  *  AND LOW TWO THETA RANGE.  THIS IS ACCOMPLISHED BY      *
C  *  DRAWING TWO LINES, ONE ON EITHER SIDE OF THE DIS-      *
C  *  CONTINUOUS LINE OF AVERAGES.  WHEN THE TWO LINES       *
C  *  BEGAN TO DIVERGE OR THE AVERAGE OF THE LINES BEGINS    *
C  *  TO FALL THE DATA AT THAT POINT IS CONSIDERED BAD.      *
C  ************************************************************
      REAL A(28),BAR,BLIN,GRAPH(60,45),B(28),DOT,N,VERT(45)
      READ(5,105)VERT
      REWIND 1
      N = 450
      DATA A /' ','A','B','C','D','E','F','G','H','I','J',
     2 'K','L','M','N','O','P','Q','R','S','T','U','V','W',
     3 'X','Y','Z','*'/
      DATA BAR,BLIN/'|','_'/
      DATA DOT/'.'/
      DO 112 I =1,28
  112 B(I) = I - 1
 1000 DO 1 J=1,45
      DO 1 I=1,60
    1 GRAPH(I,J) = A(1)
      DO 2 I=1,45
      GRAPH(1,I) = BAR
    2 GRAPH(60,I) = BAR
      DO 3 I=1,60
      GRAPH(I,1) = BLIN
    3 GRAPH(I,45) = BLIN
    4 READ(1,20,END=100)SINSQ,RINDX
      I = N * (SINSQ*.5) + 1.
      J = RINDX / 4. + 1.
      IF((I.GT.60).OR.(J.GT.45))GO TO 4
      IF(GRAPH(I,J).EQ.A(28))GO TO 4
      DO 5 INDX = 1,28
```

```
      IF(BAR.EQ.GRAPH(I,J))GO TO 6
      IF(BLIN.EQ.GRAPH(I,J))GO TO 6
      IF(A(INDX).EQ.GRAPH(I,J))GO TO 6
    5 CONTINUE
      GO TO 4
    6 GRAPH(I,J) = A(INDX + 1)
      GO TO 4
  100 WRITE(6,103)
      DO 110 I=1,60
      XNUM = 0.0
      XDEN = 0.0
      DO 111 J=1,45
      DO 111 L=1,28
      IF(GRAPH(I,J).EQ.A(L))XNUM = XNUM+B(L)*J
  111 IF(GRAPH(I,J).EQ.A(L)) XDEN = XDEN + B(L)
      IF(XDEN.EQ.0.)GO TO 110
      NAVG = XNUM / XDEN + 1.
      GRAPH(I,NAVG) = DOT
  110 CONTINUE
      DO 101 J=1,45
      JJ = (J-1) * 4
  101 WRITE(6,102)(GRAPH(I,J),I=1,60),JJ,VERT(J)
      DO 7 I=1,61
      XC = I
      SINSQ = XC/N
      SI = SQRT(SINSQ)
      SII = ARSIN(SI)* 229.183
    7 WRITE(6,104)I,SINSQ,SII
      N = N + 200.
      REWIND 1
      IF(N.GT.2200.)STOP
      GO TO 1000
   20 FORMAT(21X,F10.4,30X,F10.4)
  102 FORMAT(30X,60A1,1X,I3,2X,1A1)
  103 FORMAT(1H1,////////,25X,'SINE **2 THETA',/)
  104 FORMAT(I4,2F10.4)
  105 FORMAT(45A1)
      END
```

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