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THE CRYSTAL STRUCTURE DETERMINATIONS OF 2,2'-BIPYRIDYL-
AMINE AND THREE COPPER(II) COMPLEXES WITH
2,2'-BIPYRIDYLAMINE

Ph. D. Thesis Submitted to Iowa State University,
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The crystal structure determinations of 2,2'-bipyridylamine
and three copper (II) complexes with 2,2'-bipyridylamine

by

John Emil Johnson

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TABLE OF CONTENTS

	Page
ABSTRACT	vi
INTRODUCTION	1
THE STRUCTURE OF BIS(2,2' BIPYRIDYLAMINE) COPPER(II) PERCHLORATE	3
Introduction	3
Experimental	4
Solution and Refinement of the Structure	6
Description of the Structure	7
Discussion	23
THE STRUCTURE OF DI(IODOBIS(2,2' BIPYRIDYLAMINE) COPPER(II) IODIDE PERCHLORATE	27
Introduction	27
Experimental	27
Solution of the Structure	29
Description of the Structure and Discussion	34
THE STRUCTURE OF DIISOTHIOCYANATOBIS (2,2' BIPYRIDYLAMINE) COPPER(II) ISOTHIOCYANATOBIS (2,2' BIPYRIDYLAMINE) COPPER(II) PERCHLORATE	55
Introduction	55
Experimental	55
Solution of the Structure	57
Description of the Structure and Discussion	71

	Page
THE STRUCTURE OF 2,2'BIPYRIDYLAMINE	82
Introduction	82
Experimental	82
Solution and Refinement	84
Description of the Structure and Discussion	95
LITERATURE CITED	102
ACKNOWLEDGMENTS	105
APPENDIX A: DIRECT PHASE DETERMINATION BY USE OF LINEAR PROGRAMMING	106
Introduction	106
Theory	107
Experimental	110
Discussion	111
APPENDIX B: RESEARCH PROPOSALS	113

The crystal structure determinations of 2,2'-bipyridylamine
and three copper(II) complexes with 2,2'-bipyridylamine

John Emil Johnson

Under the supervision of R. A. Jacobson
From the Department of Chemistry
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The structure of bis(2,2'-bipyridylamine) copper(II) perchlorate has been determined by three dimensional X-ray analysis ($\text{Cu}(\text{C}_{10}\text{H}_9\text{N}_3)_2(\text{ClO}_4)_2$, $\text{C}_{2/c}$, $a = 9.35$, $b = 12.88$, $c = 19.69$ Å, $\beta = 102.8^\circ$, $Z = 4$). The structure was refined to a final discrepancy factor of $R = 9.4\%$. The two-fold axis of the space group is utilized by the complex with pyridine nitrogens coordinating to the copper in a pseudo tetrahedral arrangement. The Cu-N bond lengths are 1.94 and 1.99 Å with the dihedral angle between the two N-Cu-N planes of 55.6° .

Distorted trigonal bipyramidal coordination geometry was found in the single crystal X-ray analysis of di(iodobis(2,2'-bipyridylamine) copper(II)) iodide perchlorate ($(\text{Cu}(\text{C}_{10}\text{H}_9\text{N}_3)_2\text{I})_2\text{IClO}_4$, $\text{P}_{2_1/c}$, $a = 19.22$, $b = 13.47$, $c = 19.50$ Å, $\beta = 11.87$, $Z = 4$). Nitrogen atoms from two different bidentate ligands and an iodine atom occupy the equatorial positions with the remaining nitrogens at the axial positions. The Cu-N distances range from 1.98 to 2.09 Å with a tendency toward elongation of the metal-equatorial nitrogen bonds relative to the axial bonds. The structure was refined by block diagonal least squares technique to a discrepancy factor of 8.60%.

The co-crystallized complexes diisothiocyanato-bis(2,2'-bipyridylamine) copper(II) and isothiocyanato-bis(2,2'-bipyridylamine) copper(II) perchlorate ($\text{Cu}(\text{C}_{10}\text{H}_9\text{N}_3)_2 (\text{NCS})_2$, $\text{Cu}(\text{C}_{10}\text{H}_9\text{N}_3)_2 \text{NCSClO}_4$, $P_{21/c}$ $a = 12.82$, $b = 14.51$, $c = 19.44$ Å, $\beta = 93.80^\circ$) display tetragonally distorted and square pyramidal geometries respectively. The octahedrally coordinated copper(II) atom occupies a centrosymmetric position of the space group with the bidentate ligands and the isothiocyanate groups coordinated trans to each other, the Cu-N isothiocyanate distance being 2.55 Å and distances of 2.01 and 2.02 Å to the bidentate ligand nitrogens. The square pyramidal copper(II) complex occupies a four-fold general position with three nitrogens from the bidentate ligands and the nitrogen of the isothiocyanate group occupying the base positions and the remaining nitrogen at the apex. The structure was refined to a crystallographic discrepancy factor of $R = 14.0\%$.

Hydrogen bonded molecules of 2,2'-bipyridylamine form dimeric units possessing two-fold crystallographic symmetry in the low melting polymorph of this compound. The structure was solved by direct methods and refined to a discrepancy factor of 6.2% using all 807 reflections measured ($\text{C}_{10}\text{H}_9\text{N}_3$, P_{ccn} , $a = 18.416$, $b = 12.294$, $c = 7.691$ Å, $Z = 8$). All nine hydrogen atoms were located and refined.

A method for direct phase determination employing linear programming is outlined and preliminary results reported.

INTRODUCTION

The crystal structures of a series of copper(II) complexes with the ligand 2,2'-bipyridylamine were determined by single crystal X-ray diffraction techniques.

In any complex containing the ligand 2,2'-bipyridylamine ligand-ligand repulsions are important and in fact essentially eliminate the possibility of a trans planar configuration without severe ligand distortion. In this way the ligand is similar to 2,2'-bipyridyl,^{1,2} but the amine ligand is more flexible and can adapt to a greater variety of geometries.

Although many copper(II) complexes have been formed containing this ligand¹ few have been characterized structurally and in some cases even the stoichiometry is in doubt. There is also considerable current interest in the electronic properties of copper(II) and their correlation with structure.³ With this in mind a series of three complexes of this type were studied and were shown to display four different coordination geometries depending on the anion present. The geometries found were: a distorted tetrahedron, a trigonal bipyramid, a square pyramid and a distorted octahedron. The first configuration occurs in $\text{CuL}_2(\text{ClO}_4)_2$ where $\text{L} = 2,2'\text{-bipyridylamine}$, the second in $(\text{CuL}_2\text{I})_2\text{IClO}_4$, and the third and fourth, respectively, in the co-crystallized complexes $\text{CuL}_2\text{NCSClO}_4$ and $\text{CuL}_2(\text{NCS})_2$.

In order to provide structural data for the free ligand, the crystal structure of the low melting polymorph of 2,2'-bipyridylamine was determined. In this crystal structure hydrogen bonds between

molecules result in discrete dimeric units possessing two-fold crystallographic symmetry.

In addition to the crystal structure work performed, a method for crystal structure determination involving linear programming is outlined in an Appendix.

THE STRUCTURE OF BIS(2,2'BIPYRIDYLAMINE)

COPPER(II) PERCHLORATE

Introduction

The crystal structure determination of bis(2,2'bipyridylamine) copper(II) perchlorate⁴ was undertaken because of the dearth of structural information available on coordination complexes with the 2,2'bipyridylamine ligand¹ and due to the conflicting evidence regarding the coordination geometry of the copper(II) perchlorate complex.⁵ While a previous crystal structure determination involving this ligand has been reported,⁶ the amine protons of the ligand had been removed in the formation of a neutral palladium complex leaving the ligand with a net charge in the square planar complex.⁷ The present study is the first report of an X-ray single crystal structure determination of a complex with the neutral ligand.

Previous X-ray powder diffraction studies show that $\text{CuL}_2(\text{ClO}_4)_2$ ($\text{L} = 2,2'\text{bipyridylamine}$) is isomorphous with $\text{ZnL}_2(\text{ClO}_4)_2$ in which zinc is presumably in a tetrahedral environment.⁵ Infrared and electronic spectral studies have indicated, however, that while the perchlorate anion is not coordinated, there is no evidence for gross departure from a planar geometry about the copper.^{4,5} Of additional interest is a comparison between this structure and that of the palladium complex, revealing two, quite different, means of relieving the steric strain in trans-coordinated ligands of this type.

Experimental

Bis(2,2'-bipyridylamine) copper(II) perchlorate was prepared as follows: 0.013 moles of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 12.5 ml of absolute ethanol. To this was added a solution of 0.027 moles 2,2'-bipyridylamine dissolved in 175 ml of acetone. Deep blue microcrystals precipitated immediately. The copper complex was then recrystallized using hot water. On slow cooling very small blue plate-like crystals and larger rod-like crystals were formed. Although the latter crystals did not have well formed faces, they were found to be single crystals and were used for this investigation. Weissenberg photographs taken of the plate-like crystals indicate that the unit cells of the two types of crystals are identical. Preliminary Weissenberg photographs exhibited 2/m Laue symmetry, indicating a monoclinic space group.

Crystal Data. -- $\text{C}_{20}\text{H}_{18}\text{N}_6\text{CuCl}_2\text{O}_8$, $M = 604.9$, monoclinic, $a = 9.35 \pm 0.02$, $b = 12.88 \pm 0.01$, $c = 19.69 \pm 0.02$ Å, $\beta = 102.8 \pm 0.3^\circ$, $V = 2313$ Å³, $D_m = 1.74$ g/cc, $D_c = 1.74$ g/cc, $Z = 4$, $F(000) = 1288$ e, $\mu = 12.8$ cm⁻¹, for Mo K α radiation. Space group Cc (C_s^4) or C2/c (C_{2h}^6) from systematic absences hkl for $h+k=2n+1$, and $h0l$ for $l=2n+1$.

The unit cell parameters were determined from the 2θ values of high order reflections whose centers were determined from left-right, top-bottom beam splitting on a previously aligned Hilger-Watts four circle diffractometer. (Mo K α radiation, $\lambda = .7107$ Å)

For data collection, a crystal having approximate dimensions 0.2 x 0.12 x 0.12 mm was mounted with the elongated direction (b axis) along the spindle axis of the goniometer head. Data were collected

at room temperature utilizing an automated Hilger-Watts four circle diffractometer equipped with a scintillation counter and using Zr-filtered Mo K α radiation. Within a 2θ sphere of 40° , all data in each of two octants were recorded using a θ - 2θ scan technique. The steps were 0.01° in θ and the counting time per step was 0.4096 sec. The symmetric scan range consisted of fifty steps plus two steps per degree 2θ . Stationary crystal, stationary counter background counts of one half the total scan time were made at the beginning and end of each scan.

As a general check on crystal and electronic stability, the intensities of three large reflections (222, 006, and 131) were re-measured periodically during the data collection period. No significant decrease in intensities was detected during the data collection period for these intensities and therefore no correction was made for crystal decomposition.

The intensity data were corrected for Lorentz-polarization effects, but no correction was made for absorption since $\mu = 12.80 \text{ cm}^{-1}$, with associated maximum and minimum transmission factors of 0.86 and 0.77.

Equivalent reflections were averaged to yield 2078 independent intensities. The estimated error in the intensity was calculated from

$$[\sigma(I)]^2 = \frac{C_T}{I} + \frac{C_B}{I} + \left(\frac{K_T C_T}{I}\right)^2 + \left(\frac{K_B C_B}{I}\right)^2$$

where $\underline{C}_T$ and $\underline{C}_B$ are the total count and background count, respectively. $\underline{K}_T$ and $\underline{K}_B$ are the fractional random errors in $\underline{C}_T$ and $\underline{C}_B$, respectively, and were both assigned values of .05. The estimated standard deviation in the structure factor was calculated from $\sigma(\underline{I})$ by the finite difference method.⁸ Of all the independent reflections measured, 1167 had $\underline{I} \geq 3\sigma(\underline{I})$ and these were considered observed.

Solution and Refinement of the Structure

A Patterson map⁹ was computed and analysis indicated that the probable space group was C_2/c with the copper atom occupying a position of two-fold crystallographic symmetry. The centrosymmetric space group was also indicated by a statistical test¹⁰ and later confirmed by successful refinement in this space group. Initial positions for the copper and chlorine atoms were determined from this Patterson map and the remaining atoms were found from successive electron density map calculations. The atoms were refined first isotropically and then, since evidence of anisotropic motion was evident from a difference Fourier map, anisotropically to a final conventional discrepancy factor of $R = 9.4\%$ and a weighted discrepancy factor

$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 9.4\%$. Scattering factors used were those of Hansen *et al.*¹¹ with copper and chlorine atoms modified for the real and imaginary parts of anomalous dispersion.¹² During the latter stages of refinement, 31 reflections where $|F_o| \leq \frac{1}{2}|F_c|$ were removed and the weights were checked by an $\frac{1}{w\Delta^2}$ plot against $|\bar{F}_o|$, and subsequently, slightly modified to give a more constant value of

$\overline{\Delta^2}$. A difference electron density map at this stage indicated that all nonhydrogen atom positions had been accounted for. It was impossible to determine hydrogen positions from the map; however, the positions of the aromatic hydrogen positions were calculated assuming a benzoid geometry and treated as parameters in the final least squares refinement. A carbon hydrogen distance of 1.05 Å was assumed and the atoms were assigned an isotropic temperature factor of 6.0 Å².

The final standard deviation for an observation of unit weight $[\sum \Delta^2 / (NO - NV)]^{1/2}$, where $\Delta = |F_o| - |F_c|$, NO is the number of observations (1135) and NV is the number of variables (168), was 0.97 electrons. During the final cycle of least squares the largest shift in any parameter was less than 0.2 times its standard deviation. The final values of positional and thermal parameters are listed in Tables I and II, along with their standard deviations as derived from the inverse matrix of the final least squares cycle.¹³ In Figure 1 are listed the magnitudes of the observed and calculated structure factors in electrons x 10. The computer drawings used throughout the text were produced by OR TEP.¹⁴ Distances and angles with their standard derivations were calculated using the variance-covariance matrix from the final least squares cycle and OR FFE program.¹⁵

Description of the Structure

The structure of bis(2,2'-bipyridylamine) copper(II) perchlorate consists of discrete monomers of the complex in which each copper atom is bound in a bidentate fashion to two ligand groups. There

Table I. Final atomic coordinates^a with estimated standard deviations^b in parenthesis

Atom	x	y	z
Cu	0.0 ^{*c}	0.1943 (1)	0.25 [*]
N(1)	-0.1738 (11)	0.1452 (8)	0.1824 (5)
N(2)	-0.0742 (11)	0.1800 (9)	0.0827 (5)
N(3)	0.9972 (12)	0.2512 (7)	0.1786 (5)
C(1)	-0.2857 (13)	0.1068 (12)	0.2075 (7)
C(2)	-0.4096 (15)	0.0711 (12)	0.1659 (7)
C(3)	-0.4330 (15)	0.0671 (11)	0.0900 (7)
C(4)	-0.3098 (15)	0.1084 (10)	0.0668 (6)
C(5)	-0.1095 (14)	0.1436 (10)	0.1109 (6)
C(6)	0.0461 (12)	0.2343 (10)	0.1082 (6)
C(7)	0.1224 (14)	0.2780 (9)	0.0608 (6)
C(8)	0.2461 (16)	0.3337 (11)	0.0857 (7)
C(9)	0.3420 (12)	0.3520 (12)	0.1611 (7)
C(10)	0.2225 (15)	0.3049 (11)	0.2404 (7)
Cl	-0.3196 (3)	0.4439 (3)	0.1075 (2)
O(1)	-0.3996 (12)	0.3643 (10)	0.0660 (5)
O(2)	-0.3955 (12)	0.4797 (8)	0.1573 (5)

^aPositional parameters are in fractional unit cell coordinates.

^bEstimated standard deviations are given in parenthesis for the least significant figures.

^cAsterisk (*) denotes an atomic parameter fixed by symmetry.

Table I (continued)

Atom	x	y	z
O(3)	-0.2961(14)	0.5263(8)	0.0650(6)
O(4)	-0.1834(12)	0.4027(9)	0.1422(6)
H(1) ^d	-0.275	0.105	0.266
H(2)	-0.499	0.043	0.189
H(3)	-0.521	0.040	0.060
H(4)	0.316	0.111	0.007
H(7)	0.082	0.267	0.005
H(8)	0.306	0.367	0.050
H(9)	0.398	0.394	0.179
H(10)	0.263	0.314	0.264

^d Positions calculated for aromatic hydrogen atoms. The number of the hydrogen atom corresponds to the carbon atom to which it is bonded. All hydrogen atoms have been assigned an isotropic temperature factor of 6.0 Å².

Table II. Anisotropic temperature^a factors with standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	706(30)	604(19)	136(6)	00*	135(12)	00*
N(1)	839(156)	412(73)	167(30)	-56(95)	132(57)	-10(42)
N(2)	966(167)	763(101)	215(34)	-358(114)	289(64)	103(50)
N(3)	974(170)	518(83)	191(32)	11(106)	224(61)	46(45)
C(1)	637(193)	571(109)	334(51)	-213(127)	226(83)	-10(64)
C(2)	1061(230)	796(132)	305(51)	-33(160)	280(92)	43(73)
C(3)	1016(207)	728(123)	252(45)	-222(146)	196(80)	-47(65)
C(4)	1033(211)	410(104)	243(43)	-117(131)	-31(83)	-111(57)
C(5)	1066(209)	353(92)	220(41)	-66(120)	188(77)	32(56)
C(6)	399(143)	485(95)	176(37)	69(111)	68(59)	-14(52)
C(7)	800(177)	376(93)	221(39)	-78(116)	200(71)	52(52)
C(8)	1174(231)	467(112)	319(50)	49(136)	303(87)	3(61)
C(9)	851(194)	730(117)	259(45)	-140(135)	256(79)	11(64)
C(10)	950(200)	523(103)	338(50)	-299(139)	236(86)	134(69)
Cl	984(51)	527(27)	208(10)	-97(32)	210(20)	3(14)
O(1)	1942(199)	1260(113)	328(38)	-763(130)	234(70)	-331(58)
O(2)	2056(199)	831(92)	402(41)	3(121)	567(79)	-49(53)
O(3)	2446(240)	785(98)	633(54)	349(130)	744(99)	369(63)
O(4)	1176(178)	893(100)	570(51)	245(120)	109(76)	176(60)

^a β 's $\times 10^5$; the form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Figure 1. Observed and calculated structure factors ($\times 10$) for
bis(2,2'-bipyridylamine) copper(II) perchlorate

is no indication of coordination of the perchlorate group, the closest oxygen copper distance being 3.6 Å.

The copper atom lies on the crystallographic two-fold axis and therefore the exact point group symmetry of the cation is C_2 . However, the geometry can best be described as a distorted tetrahedron (Figure 2) with point group symmetry being nearly D_{2d} if only the atoms bound to the copper are considered. The significant bond distances and angles are given in Table III, with significant nonbonded distances in Table IV. Figure 4 is a stereoscopic view of the unit cell.

The two independent copper-nitrogen distances are somewhat different, 1.94(1) vs 1.99(1) Å. This difference probably results from steric effects evident in other parts of the molecule and has been observed in a similar 2,2'-bipyridyl complex of copper(II).¹⁶ The copper-amine nitrogen distance is 3.19 Å, indicating no appreciable interaction between these atoms. The bond distances within the 2,2'-bipyridylamine ligand are similar to those reported in the palladium complex involving this ligand. The closest approach between carbon atoms of different ligands is 3.06 Å between C(1) and C(10) (Table IV). The distance between the associated hydrogen atoms is 2.76 Å, indicating that the geometry of the cation has reduced interligand crowding. The mean carbon-carbon and carbon-nitrogen bond distances in the pyridine groups of the ligand are 1.40 and 1.35 Å, respectively. These averages agree quite well with those reported for pyridine.¹⁷ There is distortion about the bridging nitrogen as evidenced by the

Figure 2. A view displaying the pseudotrahedral geometry of the bis(2,2'-bipyridylamine) copper(II) moiety

Table III. Bond lengths (angstroms) and bond angles (degrees) with estimated standard deviations in parentheses

<u>Distances</u>			
N(1)-C(1)	1.35(1)	N(2)-C(5)	1.41(1)
C(1)-C(2)	1.33(2)	N(2)-C(6)	1.32(1)
C(2)-C(3)	1.45(2)		
C(3)-C(4)	1.44(2)	Cu-N(1)	1.94(1)
C(4)-C(5)	1.32(2)	Cu-N(3)	1.99(1)
C(5)-N(1)	1.37(2)		
C(6)-C(7)	1.41(2)		
C(7)-C(8)	1.35(2)		
C(8)-C(9)	1.47(2)	Cl-O(1)	1.41(1)
C(9)-C(10)	1.41(2)	Cl-O(2)	1.41(1)
C(10)-N(3)	1.33(1)	Cl-O(3)	1.39(1)
C(6)-N(3)	1.37(2)	Cl-O(4)	1.40(1)
<u>Angles</u>			
N(1)-C(1)-C(2)	123(1)	C(5)-N(2)-C(6)	134(1)
C(1)-C(2)-C(3)	122(1)	N(3)-Cu-N(1)	95.6(4)
C(2)-C(3)-C(4)	112(1)	N(1)-Cu-N(1) ^a	142.0(6)
C(3)-C(4)-C(5)	123(1)	N(3)-Cu-N(3) ^a	137.3(6)
C(4)-C(5)-N(1)	123(1)	O(1)-Cl-O(2)	110(1)
C(5)-N(1)-C(1)	117(1)	O(1)-Cl-O(3)	110(1)
C(6)-C(7)-C(8)	120(1)	O(1)-Cl-O(4)	108(1)

^aPrimed atom numbers refer to atoms primed in Figure 3.

Table III (continued)

<u>Angles</u>			
C(7)-C(8)-C(9)	123 (1)	O(2)-C1-O(3)	110(1)
C(8)-C(9)-C(10)	113 (1)	O(2)-C1-O(4)	109(1)
C(9)-C(10)-N(3)	118(1)	O(3)-C1-O(4)	109(1)
N(3)-C(8)-C(9)	118(1)		
C(10)-N(3)-C(6)	122 (1)		

Table IV. Nonbonded interatomic distances (angstroms)

N(2) ... O(1)	3.81(2)	C(1) ... C(10 ^I) ^a	3.06(1)
N(2) ... O(2)	5.29(2)	H(1) ... H(10 ^I)	2.76
N(2) ... O(3)	4.89(2)	Cu ... O(1)	5.09(1)
N(2) ... O(4)	3.34(2)	Cu ... O(2)	5.24(1)
C(10 ^I) ... C(1 ^{III})	3.88(2)	Cu ... O(3)	5.90(1)
C(9 ^I) ... N(1 ^{III})	3.82(2)	Cu ... O(4)	3.61(1)
N(3 ^I) ... C(2 ^{III})	4.12(2)	Cu ... Cl	4.84
C(6 ^I) ... C(3 ^{III})	4.32(2)	Cu ... Cu	7.95(1)
C(8 ^I) ... C(5 ^{III})	4.07(2)	Cu ... N(2)	3.19(1)

^aThe following symmetry related positions are referred to:
 I - $x, y, \frac{1}{2} - z$; II - $\frac{1}{2} + x, \frac{1}{2} + y, z$; III - $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Figure 3. Projection of the bis(2,2'-bipyridylamine) copper(II)²⁺ moiety on the ac plane, with some relevant distances

significant difference between the two carbon-nitrogen distances, 1.41 and 1.32 Å.

Least squares plane calculations (Table V) indicate that the individual pyridine rings are essentially planar but the ligand as a whole is not with a 9.6° angle between the normals to the least squares planes of the pyridine rings.

The dihedral angle between the planes defined by N(1), Cu, N(3), and N(1)', Cu, N(3)' is 55.6° , while the dihedral angle between planes defined by N(1), Cu, N(1)', and N(3), Cu, N(3)' is 92.6° . The first dihedral angle is somewhat closer to the 90° angle expected for the tetrahedral geometry than the 0° angle expected for the square planar configuration. The chelate ring formed by Cu, N(1), C(5), N(2), C(6), N(3) is in a boat configuration with Cu and N(2) below the level of the plane defined by the other four atoms (Table V).

There appears to be no significant hydrogen bonding in the structure, the closest approach between likely atoms being 3.3 Å between N(2) and O(4) of the perchlorate group. The location of the perchlorate group relative to the amine nitrogen (Figure 4) would lead one to discount the importance of hydrogen bonding.

The cations of the complex are stacked in the y direction of the unit cell with the perchlorate sandwiched between alternate layers of the pyridyl rings (Figure 4). The closest approach between two pyridyl rings of different cations is 3.82 Å (Table IV). The closest approach between two copper atoms is 7.95 Å.

Table V. Least squares planes^a

Plane	l	m	n	k
1	-0.468	0.880	-0.079	-2.53
2	-0.409	0.911	-0.055	-2.52
3	-0.548	0.835	-0.500	-2.46
Deviations from Plane (angstroms)				
Atom	Plane 1	Plane 2	Plane 3	
Cu	-0.163 ^{*b}			
N(1)	0.00	0.00		
C(1)		0.00		
C(2)		0.02		
C(3)		0.004		
C(4)		-0.003		
C(5)	0.01	-0.012		
N(2)	-0.105 [*]			
C(6)			-0.006	
C(7)			0.001	
C(8)			0.02	
C(9)			0.005	
C(10)			-0.007	
N(3)	0.00		0.008	

^aThe planes $lX' + mY' + nZ' + k = 0$ are referred to orthogonal axes. The transformation from fractional cell coordinates (x, y, z) is $X' = ax + cz(\cos\beta)$, $Y' = yb$, $Z' = zV/ab$.

^bStarred values correspond to atoms not used in the least squares plane calculation.

Discussion

The geometry about the copper in this complex can best be described as a tetrahedron which has been compressed along the crystallographic two-fold axis to give the observed geometry; this geometry probably results from steric interaction between the ligands.

The original reflectance spectra was interpreted as resulting from a square planar or tetragonally distorted geometry. In a recent analysis of the spectra, Lancaster proposed that the reflectance spectra would be consistent with a nonplanar geometry if the high frequency peak at 18.11 KK were not, in fact, a $d \rightarrow d$ transition, but of some other origin such as charge transfer.⁵ Dudley *et al.*¹⁸ have reported the single crystal polarized spectra, however, and conclude that the peak at 18.11 KK is a $d \rightarrow d$ transition and, from the electronic properties, propose that the observed stereochemistry results from a tetrahedrally distorted square planar geometry.

It is of interest to compare the structure of the bipyridylamine copper complex with that of the bipyridylaminato palladium complex. Both crystallize in the same space group, but the palladium occupies a $\bar{1}$ symmetry site, while the copper atom is on a two-fold site. The mechanism invoked to reduce the steric hindrance between the two ligands in each complex is quite different. In the palladium complex the ligand bends about the bridging nitrogen such that the dihedral angle between the pyridine rings is 38.2° , while the coordination geometry is strictly square planar. In the copper complex, however, a more tetrahedral geometry is assumed, allowing the ligand as a whole

to be nearly planar with only a 9.8° dihedral angle between the pyridine rings. The pyridine rings are somewhat less distorted from planarity in the copper relative to the palladium moiety, maximum deviations being .02 in the former compared to .04 Å in the latter. There is, however, more variation in the carbon-bridging nitrogen distances in the copper complexes relative to those in the palladium moiety: 1.41 and 1.32 vs 1.37 and 1.33 Å, respectively, and the C-N-C angle in the copper salt (134°) shows greater distortion from the expected value than that found in the more aromatic palladium compound (123°).

Figure 4. Stereoscopic view of the packing in the unit cell of bis(2,2'-bipyridylamine) copper(II) perchlorate. The origin is at the bottom left hand corner of the enclosure, and z lies across the page, x upward, and y out of the page

THE STRUCTURE OF DI(IODOBIS(2,2'BIPYRIDYLAMINE)
COPPER(II)) IODIDE PERCHLORATE

Introduction

The crystal and molecular structure of di(iodobis(2,2'bipyridylamine) copper(II)) iodide perchlorate was undertaken to provide additional structural data on the coordination of 2,2'bipyridylamine with copper(II) in the presence of various anions. The compound $(\text{CuL}_2\text{I})_2\text{IClO}_4$ was prepared by the method reported by McWhinnie⁴ for $\text{CuL}_2\text{IClO}_4$. A recent study of the visible, infrared and electron spin resonance spectra of the latter compound indicated a five coordinate copper(II) species and a square pyramidal geometry was postulated.⁵

Experimental

The preparation given by McWhinnie for $\text{CuL}_2\text{IClO}_4$ was followed;⁴ although the reaction appeared to proceed as had been reported and small dark green crystals similar to those reported by McWhinnie were obtained, analysis, later confirmed by the single crystal X-ray investigation, indicated a greater percentage of iodine (28.5% compared to 20%) than expected for the simple stoichiometry $\text{CuL}_2\text{IClO}_4$. The crystals, however, displayed a reflectance spectra similar to that reported by McWhinnie.

Crystal Data. -- $\text{C}_{40}\text{N}_{12}\text{H}_{36}\text{Cu}_2\text{I}_3\text{ClO}_4$, $M = 1292$ g/m, monoclinic, $a = 19.21 \pm .01$, $b = 13.47 \pm .01$, $c = 19.50 \pm .05$ Å, $\beta = 11.88 \pm .15^\circ$, $V = 4687$ Å³, $D_m = 1.85$ g/cc, $Z = 4$, $D_c = 1.83$ g/cc, $F(000) = 2504$ e,

space group $P2_{1/c}$, (C_{2h}^5) from systematic absences $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$, Mo - K_{α} X-radiation, $\lambda = .7107 \text{ \AA}$, $\mu(\text{Mo} - K_{\alpha}) = 29.47 \text{ cm}^{-1}$.

The unit cell parameters and their standard deviations were determined by a least squares fit to twelve independent reflection angles whose centers were determined by left-right top-bottom beam splitting on a previously aligned Hilger and Watts four-circle diffractometer.¹⁹ Any error in the instrumental zero was eliminated by centering the reflection at both $+2\theta$ and -2θ . For data collection a crystal having approximate dimensions $0.25 \times 0.25 \times 0.15 \text{ mm}$ was mounted with the b axis aligned along the spindle axis of the goniometer.

Data were collected at room temperature utilizing a Hilger and Watts four-circle diffractometer equipped with scintillation counter and using Zr-filtered MoK_{α} radiation. Within a 2θ sphere of 40° , all data in the hkl and $\bar{h}k\bar{l}$ octants were collected using a stationary counter-stationary crystal technique. Intensities were measured by counting at the peak center $\theta(hkl)$ for ten seconds and subtracting two five-second background counts at $\theta(hkl) \pm [0.25 + .01 \times \theta(hkl)]$. A total of 8477 reflections were measured in this manner. Also 100 reflections covering a range of $\sin \theta/\lambda$ values were remeasured via the step scan method (moving-crystal moving-counter) for later use in a peakheight to stepscan conversion.²⁰ The plot of the ratio of $I_{\text{integrated}}/I_{\text{peakheight}}$ vs $\sin \theta/\lambda$ of these reflections increased

smoothly from 0.95 at low values of $\sin \theta$ to 1.60 at large values and no χ or ϕ dependencies were indicated.

As a general check on electronic and crystal stability, the intensity of three large reflections (551, 600, 004) were checked periodically during the data collection. No significant decrease in the intensity of these reflections was observed. The intensities were corrected for Lorentz-polarization effects, but no absorption correction was deemed necessary.

Equivalent reflections were averaged to yield 8259 independent intensities. The estimated error in each intensity was calculated from

$$[\sigma(I)]^2 = \underline{C}_t + \underline{C}_b + (\underline{K}_t \underline{C}_t)^2 + (\underline{K}_b \underline{C}_b)^2$$

where $\underline{C}_t$ and $\underline{C}_b$ are the total and background counts, $\underline{K}_t$ and $\underline{K}_b$ are estimates for nonstatistical errors in $\underline{C}_t$ and $\underline{C}_b$ and both were assigned values of .05. The estimated deviations in the structure factors were calculated from the finite difference method.⁸ Of all the measured independent reflections, 3921 had $I \geq 3 \sigma(I)$ and these were considered observed and used for the structure determination.

Solution of the Structure

A sharpened Patterson map²¹ was computed and initial positions of the two copper atoms and three iodine atoms were determined. A structure factor calculation with these atoms and the chlorine atom produced a conventional discrepancy

factor of 27.8%. The remaining atoms were located from successive structure factor and electron density map calculations, except for the perchlorate oxygen atoms which could not be located or refined because of severe disorder. With all the atoms isotropic, the structure refined at $R = 12.5\%$. At this point a difference electron density map indicated anisotropic motion, especially about the copper and iodine atoms. Refinement with these heavy atoms anisotropic produced an R factor of 9.16%. The perchlorate oxygen atoms were taken into account by allowing both the occupation parameter and the isotropic temperature factor of the chlorine to increase. All atoms, except the chlorine, were now refined with anisotropic temperature factors. The discrepancy factor at this stage was 8.80%. A difference electron density map at this stage showed no significant peaks other than some diffuse electron density in the area of the perchlorate.

Hydrogen positions for the aromatic rings were calculated assuming a benzoid structure with a C-H distance of 1.05 Å. The hydrogen atoms were assigned the isotropic temperature factor of the attached carbon. A final structure factor calculation with these atoms present produced a discrepancy factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ of 8.63% and a weighted discrepancy factor $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 9.8%. The scattering factors used are those of Hansen *et al.*,¹¹ with copper, iodine, and chlorine modified for the real and imaginary parts of anomalous dispersion.¹² Due to the large number of variables, block diagonal least squares was used throughout.²² In Figure 5 are listed the magnitudes of the observed and calculated structure factors in

Figure 5. Observed and calculated structure factors ($\times 10$)

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1219	1220	1221	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Figure 5 (Continued)

electrons $\times 10$. The final positional parameters and anisotropic thermal parameters for nonhydrogen atoms are given in Tables VI and VII respectively, and the calculated hydrogen positions are listed in Table VIII.

Description of the Structure and Discussion

The crystal and molecular structure of di(iodobis(2,2'-bipyridyl-amine) copper(II)) iodide perchlorate consists of two crystallographically-independent five-coordinate copper(II) moieties in the asymmetric unit along with nonbonded iodide and perchlorate anions. The two five-coordinate species are both slightly distorted trigonal bipyramids with no structurally significant differences between them.

The geometry and chemical constitution of chromophore I is shown in Figure 6 while Figure 7 is a view of the asymmetric unit displaying the two cations, the iodide and the chloride ion of the perchlorate group. Table IX lists all distances and angles about the two copper atoms and the mean distances for chemically equivalent bonds within the ligands. In the following discussion all structural data quoted will be for chromophore I (containing Cu(I) and I(I)), with the equivalent data for chromophore II in parenthesis where significant.

The equatorial atoms of each trigonal bipyramid consists of two nitrogen atoms from different bidentate ligands and an iodine atom, all of which lie within $.01 \text{ \AA}$ of the equatorial plane containing the copper(II) ion. The axial positions are occupied by the remaining

Table VI. Final atomic coordinates with estimated standard deviations in parentheses^a

Atom	x	y	z
I(1)	.3214(1)	.0794(1)	.4382(1)
I(2)	.033(1)	.4096(1)	.1820(1)
I(3)	-.1767(1)	.3858(1)	.4414(1)
Cu(1)	.3855(1)	.1652(2)	.3526(1)
Cu(2)	.0540(1)	.6094(2)	.1897(1)
Cl(1)	.5274(2)	.0373(3)	.1663(2)
N(1)	.3493(9)	.2958(11)	.3739(9)
N(2)	.4554(9)	.3206(12)	.4794(9)
N(3)	.4936(9)	.2246(13)	.4005(10)
N(4)	.3595(9)	.1923(11)	.2420(9)
N(5)	.3180(10)	.0285(11)	.2089(9)
N(6)	.4144(9)	.0300(12)	.3312(9)
N(7)	.1226(9)	.5897(11)	.1362(10)
N(8)	.0250(10)	.6185(15)	.0183(10)
N(9)	-.0083(9)	.7087(13)	.1102(10)
N(10)	.1244(11)	.7053(14)	.2642(10)
N(11)	.0870(10)	.6324(14)	.3599(10)
N(12)	-.0143(8)	.6162(12)	.2473(8)
C(1)	.2777(12)	.3233(17)	.3333(14)

^aIn this and succeeding tables, estimated standard deviations are given for the least significant figures.

Table VI (continued)

Atom	x	y	z
C(2)	.2403 (13)	.3964 (17)	.3488 (13)
C(3)	.2763 (14)	.4471 (18)	.4151 (13)
C(4)	.3485 (14)	.4181 (18)	.4589 (12)
C(5)	.3847 (11)	.3427 (15)	.4358 (11)
C(6)	.5116 (11)	.2867 (15)	.4594 (12)
C(7)	.5854 (12)	.3165 (17)	.4948 (13)
C(8)	.6406 (13)	.2873 (18)	.4691 (16)
C(9)	.6233 (13)	.2246 (19)	.4093 (16)
C(10)	.5463 (12)	.1939 (18)	.3769 (14)
C(11)	.3696 (12)	.2852 (17)	.2197 (13)
C(12)	.3477 (13)	.3133 (16)	.1426 (13)
C(13)	.3131 (15)	.2424 (18)	.0938 (12)
C(14)	.2990 (13)	.1514 (16)	.1144 (10)
C(15)	.3237 (10)	.1269 (14)	.1889 (11)
C(16)	.3763 (12)	-.0169 (13)	.2705 (12)
C(17)	.3882 (14)	-.1188 (16)	.2630 (14)
C(18)	.4421 (14)	-.1669 (17)	.3206 (15)
C(19)	.4870 (15)	-.1172 (16)	.3828 (14)
C(20)	.4720 (14)	-.0212 (18)	.3869 (15)
C(21)	.1931 (12)	.5670 (14)	.1738 (16)
C(22)	.2368 (13)	.5352 (19)	.1430 (14)

Table VI (continued)

Atom	x	y	z
C(23)	.2131(14)	.5227(19)	.0661(16)
C(24)	.1398(15)	.5512(18)	.0273(13)
C(25)	.0942(12)	.5845(15)	.0582(11)
C(26)	-.0173(13)	.6941(15)	.0360(12)
C(27)	-.0655(15)	.7493(21)	-.0207(14)
C(28)	-.1010(19)	.8293(19)	.0002(19)
C(29)	-.0937(14)	.8450(19)	.0700(17)
C(30)	-.0449(15)	.7856(23)	.1229(14)
C(31)	.1623(14)	.7739(22)	.2466(18)
C(32)	.2113(14)	.8369(21)	.2944(16)
C(33)	.2248(18)	.8261(17)	.3659(15)
C(34)	.1819(14)	.7639(20)	.3897(14)
C(35)	.1320(11)	.6990(19)	.3334(15)
C(36)	.0146(11)	.6085(17)	.3211(12)
C(37)	-.0287(14)	.5788(21)	.3576(15)
C(38)	-.1023(14)	.5665(23)	.3240(15)
C(39)	-.1326(12)	.5790(19)	.2431(15)
C(40)	-.0852(12)	.6008(16)	.2118(12)

Table VII. Anisotropic thermal parameters^a

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{23}$	$10^4\beta_{13}$	$10^4\beta_{12}$
I(1)	59(1)	64(1)	40(1)	-23(1)	61(12)	-40(2)
I(2)	69(1)	55(1)	30(1)	-2(1)	38(1)	-21(2)
I(3)	64(1)	95(1)	37(1)	11(2)	38(1)	-10(2)
Cu(1)	34(1)	51(2)	25(1)	0(2)	22(2)	2(2)
Cu(2)	37(1)	61(2)	24(1)	-2(2)	28(2)	-9(2)
Cl	6.57(13) ^b	0	0	0	0	0
N(1)	35(8)	54(11)	28(7)	-28(14)	9(12)	-18(14)
N(2)	32(7)	53(12)	31(7)	3(14)	24(12)	13(14)
N(3)	35(8)	70(14)	38(8)	19(16)	30(13)	0(16)
N(4)	35(7)	37(10)	36(7)	-7(13)	50(12)	-37(13)
N(5)	48(8)	33(11)	30(7)	20(13)	22(12)	6(15)
N(6)	40(8)	64(13)	26(7)	23(15)	22(12)	17(16)
N(8)	49(7)	105(11)	41(16)	-17(13)	57(13)	-12(15)
N(9)	26(7)	85(15)	40(8)	-24(18)	16(13)	3(16)
N(10)	55(9)	90(16)	29(8)	25(17)	44(14)	-26(19)
N(11)	45(9)	93(17)	40(9)	4(14)	42(14)	-25(18)
N(12)	25(7)	81(14)	24(14)	-27(15)	27(10)	-18(15)
C(1)	42(11)	76(19)	50(10)	12(22)	51(17)	30(23)
C(2)	46(11)	82(21)	36(9)	19(22)	21(18)	23(24)
C(3)	53(11)	101(21)	32(9)	4(22)	51(22)	45(24)
C(4)	69(13)	99(21)	34(9)	-5(22)	92(19)	1(25)

^aIn the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl + \beta_{13}hl + \beta_{12}hk)]$.^bIsotropic temperature factor.

Table VII (continued)

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{23}$	$10^4\beta_{13}$	$10^4\beta_{12}$
C(5)	28(8)	60(15)	28(8)	-11(17)	35(14)	-20(18)
C(6)	34(9)	48(15)	33(9)	59(19)	-12(15)	-14(18)
C(7)	27(9)	77(18)	46(11)	53(22)	-18(16)	-25(20)
C(8)	35(11)	75(20)	86(17)	36(29)	40(22)	2(21)
C(9)	41(11)	104(24)	75(15)	-3(30)	70(22)	-6(25)
C(10)	38(10)	93(21)	51(12)	37(24)	50(19)	16(22)
C(11)	34(9)	83(20)	41(11)	-22(22)	24(17)	23(21)
C(12)	61(12)	62(17)	43(11)	54(21)	58(19)	28(22)
C(13)	89(15)	77(18)	22(9)	-2(20)	43(20)	-24(27)
C(14)	60(12)	85(18)	9(7)	-26(18)	28(15)	11(23)
C(15)	25(7)	49(14)	34(9)	4(18)	22(14)	-3(16)
C(16)	46(10)	32(13)	37(9)	4(17)	45(16)	-18(17)
C(17)	64(13)	53(17)	54(12)	-20(22)	60(21)	-19(23)
C(18)	66(13)	52(17)	64(14)	33(24)	60(22)	-3(24)
C(19)	80(14)	49(17)	48(11)	30(21)	69(21)	55(24)
C(20)	62(13)	79(20)	57(13)	62(25)	70(22)	27(25)
C(21)	35(10)	29(14)	94(16)	23(22)	64(21)	47(18)
C(22)	43(11)	91(20)	50(12)	-9(26)	-4(19)	78(25)

Table VII, (continued)

Atom	$10^4 \beta_{11}$	$10^4 \beta_{22}$	$10^4 \beta_{33}$	$10^4 \beta_{23}$	$10^4 \beta_{13}$	$10^4 \beta_{12}$
c(23)	40(11)	107(23)	80(16)	4(29)	87(22)	-5(25)
c(24)	82(15)	73(18)	41(11)	-31(22)	92(21)	3(26)
c(25)	41(9)	51(14)	24(8)	30(17)	18(14)	24(19)
c(26)	49(11)	48(15)	33(9)	-5(19)	3(17)	-17(20)
c(27)	69(14)	126(25)	32(11)	49(25)	29(20)	84(31)
c(28)	115(20)	64(20)	109(21)	61(32)	168(35)	52(32)
c(29)	56(13)	87(21)	85(16)	6(29)	94(24)	52(26)
c(30)	63(14)	171(32)	31(11)	-26(29)	12(20)	121(33)
c(31)	40(11)	135(28)	93(18)	33(35)	85(24)	-29(28)
c(32)	49(12)	116(25)	71(16)	80(32)	36(23)	-9(28)
c(33)	116(19)	41(17)	55(14)	10(14)	52(27)	-58(29)
c(34)	63(13)	111(24)	37(26)	-5(20)	22(20)	22(29)
c(35)	20(9)	105(22)	59(13)	-60(28)	-13(17)	-1(21)
c(36)	31(9)	81(19)	31(9)	-5(20)	23(15)	-28(20)
c(37)	49(12)	127(27)	49(13)	-22(28)	28(20)	-42(28)
c(38)	48(12)	165(31)	59(14)	28(32)	72(22)	-54(30)
c(39)	30(9)	92(21)	61(13)	29(28)	3(18)	-20(22)
c(40)	53(11)	69(17)	35(9)	-29(20)	62(17)	-37(22)

Table VIII. Fractional coordinates and isotropic thermal parameters for calculated hydrogen atoms. The atom number and temperature factor are those of the carbon atom to which it is attached

Atom	x	y	z	b
H(1)	.2490	.2819	.2840	4.51
H(2)	.1848	.4158	.3124	5.29
H(3)	.2491	.5065	.4316	4.32
H(4)	.3767	.4538	.5109	4.24
H(7)	.6001	.3628	.5427	5.32
H(8)	.6968	.3136	.4959	5.99
H(9)	.6645	.2003	.3883	5.53
H(10)	.5306	.1435	.3313	5.11
H(11)	.3946	.3508	.2607	4.14
H(12)	.3592	.3832	.1259	4.47
H(13)	.2956	.2593	.0362	5.20
H(14)	.2689	.0981	.0733	4.62
H(17)	.3559	-.1578	.2135	5.06
H(18)	.4493	-.2452	.3168	5.68
H(19)	.5318	-.1536	.4258	5.11
H(20)	.5055	.0193	.4351	4.91
H(21)	.2146	.5756	.2326	5.58
H(22)	.2935	.5172	.1770	7.15
H(23)	.2488	.4937	.0399	5.90
H(24)	.1189	.5458	-.0317	5.40

Table VIII (continued)

Atom	x	y	z	B($\text{\AA}^2$)
H(27)	-.0757	.7328	-.0773	6.77
H(28)	-.1349	.8791	-.0417	7.81
H(29)	-.1249	.9019	.0841	6.07
H(30)	-.0353	.8024	.1793	7.92
H(31)	.1540	.7811	.1894	6.25
H(32)	.2384	.8934	.2753	7.41
H(33)	.2699	.8665	.4056	7.19
H(34)	.1850	.7633	.4456	5.98
H(37)	-.0032	.5645	.4157	6.82
H(38)	-.1373	.5487	.3539	6.00
H(39)	-.1912	.5704	.2113	6.68
H(40)	-.1064	.6064	.1528	4.39

Figure 6. Chromophore I of $(\text{CuL}_2\text{I})_2\text{IClO}_4$ displaying the trigonal bipyramidal coordination geometry.

Figure 7. A formula unit of $(\text{CuL}_2\text{I})_2\text{IClO}_4$

Table IX. Bond lengths (angstroms) and bond angles (degrees) with standard deviations in parentheses

Cu(1)-N(1)	1.992(15)	Cu(2)-N(7)	1.981(13)
Cu(1)-N(6)	1.992(16)	Cu(2)-N(12)	2.024(12)
Cu(1)-N(4)	2.056(16)	Cu(2)-N(10)	2.036(17)
Cu(1)-N(3)	2.094(13)	Cu(2)-N(9)	2.060(18)
Cu(1)-I(1)	2.679(3)	Cu(2)-I(2)	2.717(3)
N(1)-Cu(1)-N(6)	175.6(10)	N(7)-Cu(2)-N(12)	174.7(10)
N(1)-Cu(1)-N(4)	95.4(10)	N(7)-Cu(2)-N(10)	93.7(11)
N(1)-Cu(1)-N(3)	86.3(10)	N(7)-Cu(2)-N(9)	90.3(11)
N(1)-Cu(1)-I(1)	88.4(7)	N(7)-Cu(2)-I(2)	87.3(8)
N(6)-Cu(1)-N(4)	85.5(10)	N(12)-Cu(2)-N(10)	88.4(11)
N(6)-Cu(1)-N(3)	97.8(11)	N(12)-Cu(2)-N(9)	94.2(10)
N(6)-Cu(1)-I(1)	88.0(8)	N(12)-Cu(2)-I(2)	87.8(7)
N(4)-Cu(1)-N(3)	102.3(10)	N(10)-Cu(2)-N(9)	99.8(11)
N(4)-Cu(1)-I(1)	137.9(7)	N(10)-Cu(2)-I(2)	135.5(8)
N(3)-Cu(1)-I(1)	119.8(8)	N(9)-Cu(2)-I(2)	124.7(8)

Ligand 1 [C(1)-C(10) N(1)-N(3)]

mean C-C 1.39(2)

mean C-N (pyridyl) 1.34(2)

mean C-N (bridge) 1.35(2)

Ligand 2 [C(11)-C(20) N(4)-N(6)]

mean C-C 1.37(2)

mean C-N (pyridyl) 1.35(2)

mean C-N (bridge) 1.42(2)

Table IX (continued)

ligand 3 [C(21)-C(30)	N(7)-N(9)]
mean C-C	1.36(2)
mean C-N (pyridyl)	1.36(2)
mean C-N (bridge)	1.39(2)
ligand 4 [C(31)-C(40)	N(10)-N(12)]
mean C-C	1.37(2)
mean C-N (pyridyl)	1.31(2)
mean C-N (bridge)	1.41(2)

two nitrogen atoms. By adopting this geometry, ligand-ligand nonbonded repulsions are minimized. The copper-nitrogen equatorial bonds appear to be slightly but significantly elongated compared to the axial ones, the average equatorial distance being 2.06 Å vs 2.00 Å for the average axial distance. This type of equatorial elongation has been observed to various degrees in other complexes of this type²³ and has been discussed by Raymond et al.²⁴ The copper-iodide distances agree well with that reported by Barclay et al.²⁵ The bound iodide atoms display pronounced anisotropic thermal motions (Figure 6); the smallest component, approximately in the direction of the copper-iodide bond, is 0.193 Å (0.201 Å) and the largest, 0.324 Å (0.350 Å), is at an angle of 41° (50°) with the equatorial plane. This pattern of motion is quite consistent with the steric restrictions imposed by the axial nitrogens and the other ligand repulsions.

The deviation from trigonal-bipyramidal geometry manifests itself primarily in angular distortions about the equator. Although the I(1)-Cu(1)-N(3) angle is normal at 119.8° (124.7°), the I(1)-Cu(1)-N(4) is 137.9° (135.5°) reducing the N(3)-Cu(1)-N(4) angle to 102.3° (99.8°).

In the ligand itself, the carbon-nitrogen bond distances within the pyridine rings average 1.34 Å while the bridging C-N distances average 1.39 Å; the carbon-carbon distances average 1.37 Å. The individual pyridine rings are planar within standard deviations. The ligands themselves are bent considerably about the bridging nitrogen atoms with dihedral angles between the pyridine rings of

33° (33°) and 37° (40°). In $\text{CuL}_2(\text{ClO}_4)_2$ the dihedral angle was found to be 9.6°; the variation in this angle illustrates the flexibility of the ligand. The six-membered chelate rings formed by the copper and the bidentate ligands are all in a boat configuration, with the copper atom 0.78 Å below the plane of the other four atoms of the ring on the average, and the bridging nitrogen 0.29 Å below this plane. The shorter nonbonded distances between atoms in the same coordination species are listed in Table V, the minimum distance being 2.80 Å between H(10) and H(20).

The nonbonded iodide is located 6.78 Å from Cu(1) and 5.52 Å from Cu(2) while the chloride of the perchlorate group is located 5.56 Å and 7.35 Å from Cu(1) and Cu(2), respectively. There are no unusually short contacts between the two chromophores, the shortest being 2.34 Å between H(14) and H(28).

There are no apparent steric effects that would lead to the nearly identical distortions from the trigonal-bipyramidal geometry displayed by both chromophores; therefore electronic effects must be considered. Hathaway and his coworkers have proposed that in the similar compound iodobis(2,2'-bipyridyl) copper(II) iodide,²⁵ the bound iodide may be occupying two coordination sites of a cis-distorted octahedron, thereby explaining the reduction of the equatorial N-Cu-N bond angle from 120° to 114°. ^{26,27} This cis-distorted geometry has been observed in nitritobis (2,2'-bipyridyl) copper(II) nitrate where the angle is 102°. ¹⁶

In Figure 8 the coordination geometries of the 2,2'-bipyridyl complexes mentioned above are schematically drawn along with that of the 2,2'-bipyridylamine complex. It should be noted that the equatorial N-Cu-N bond angles of the nitrito complex and the 2,2'-bipyridylamine iodide complex are similarly reduced.

An alternative explanation for the equatorial angular asymmetry as well as the reduction of the equatorial N-Cu-N bond angle would be that the trigonal bipyramid is distorting toward a square pyramid with N(3) at the apex. This view is supported by the large N(4)-Cu(1)-I(1) angle, while all but the N(3)-Cu(1)-I(1) angles involving N(3) are within 12° of the 90° angle expected for the square pyramid. It should also be noted that Lancaster *et al.*, on the basis of electronic spectra, had predicted a square pyramid with the iodide at the apex for iodobis (2,2'-bipyridylamine) copper(II) iodide perchlorate.⁵

Figure 8. Comparison of coordination geometries of similar 2,2'-bipyridyl complexes with that of the 2,2'-bipyridylamine complex

$[\text{Cubipy}_2\text{I}]^+$

$[\text{Cubipy}_2\text{NO}_2]^+$

$[\text{Cubipyam}_2\text{I}]^+$

Table X. Nonbonded intramolecular distances (Å)

N(1) ... N(3)	2.80	N(7) ... N(9)	2.87
H(10) ... H(20)	2.80	H(30) ... H(40)	2.93
N(1) ... N(4)	2.99	N(7) ... N(10)	2.93
N(3) ... N(6)	3.08	N(9) ... N(12)	2.99
H(1) ... H(11)	3.10	H(21) ... H(31)	3.00
Cu(1) ... N(2)	3.13	Cu(2) ... N(8)	3.15
Cu(1) ... N(5)	3.19	Cu(2) ... N(11)	3.18
I(1) ... N(6)	3.28	I(2) ... N(12)	3.33
I(1) ... N(1)	3.29	I(2) ... N(7)	3.33
N(3) ... N(4)	3.33	N(9) ... N(10)	3.13
I(1) ... N(3)	4.15	I(2) ... N(9)	4.23
I(1) ... N(4)	4.42	I(2) ... N(10)	4.41

THE STRUCTURE OF DIISOTHIOCYANATOBIS (2,2'BIPYRIDYLAMINE)

COPPER(II) ISOTHIOCYANATOBIS (2,2'BIPYRIDYLAMINE)

COPPER(II) PERCHLORATE

Introduction

As part of a series of structural investigations of metal complexes with the ligand 2,2'bipyridylamine, the preparation and structural characterization of $\text{CuL}_2\text{NCSClO}_4$ ($\text{L} = 2,2'\text{bipyridylamine}$) were undertaken. Subsequent analysis showed this to be a mixture of $\text{CuL}_2(\text{NCS})_2$ and $\text{CuL}_2\text{NCSClO}_4$.

Experimental

The preparation reported by McWhinnie for $\text{CuL}_2\text{NCSClO}_4$ was followed⁴ and the reaction appeared to proceed as expected yielding small dark green crystals as had been found by McWhinnie. However, the preliminary single crystal data were not consistent with the simple stoichiometry reported by McWhinnie. Subsequently, the crystals were shown to be a co-crystallized mixture of diisothiocyanatobis (2,2'bipyridylamine) copper(II), $[\text{CuL}_2(\text{NCS})_2]$, and isothiocyanatobis(2,2'bipyridylamine) copper(II) perchlorate, $[\text{CuL}_2\text{NCSClO}_4]$, hereafter referred to as compound I and II respectively.

Crystal Data. -- $\text{C}_{43}\text{N}_{15}\text{H}_{36}\text{Cu}_2\text{S}_3\text{ClO}_4$ $M_{\text{I}} = 522.10$ g/m, $M_{\text{II}} = 563.47$ g/m
monoclinic, $a = 12.74 \pm .02$, $b = 14.48 \pm .01$, $c = 19.33 \pm .03$ Å, $\beta = 93.84 \pm .40^\circ$, $V = 3558$ Å³, $D_m = 1.59$ g/cc, $Z_{\text{I}} = 2$, $Z_{\text{II}} = 4$, $D_c = 1.55$ g/cc,
 $F(000) = 1810$ e, space group $P_{21/c}$, $(C_{2h})^5$ from systematic

absences $h0\ell$ for $\ell = 2n+1$ and $0k0$ for $k = 2n+1$, Mo-K α X-radiation, $\lambda = 0.7107 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 11.32 \text{ cm}^{-1}$. The unit cell parameters were determined from repeated measurements of 2θ values of high order reflections whose centers were determined by left-right top-bottom beam splitting on a previously aligned Hilger and Watts four-circle diffractometer (Mo-K α radiation $\lambda = 0.7107 \text{ \AA}$). The observed density was determined by floatation in carbon tetrachloride.

A crystal having approximate dimensions .24 x .12 x .062 mm was mounted with the b axis (.24 mm) aligned along the spindle axis. Data were collected at room temperature utilizing a Hilger and Watts four-circle diffractometer equipped with a scintillation counter and using Zr-filtered MoK α radiation. Within a 2θ sphere a 40° all data in the hkl and $\bar{h}\bar{k}\bar{\ell}$ octants were recorded using a θ - 2θ step-scan technique with a take-off angle of 4.5° . Symmetric scan ranges of 1.00° in 2θ at low two-theta values to 2.00° at high two-theta values were used. Stationary crystal-stationary counter background measurements were made at the beginning and end of the scan, each measurement being made for one-half the total scan time. The counting rate was 0.2048 sec per step of 0.02° in two-theta. A total of 3501 reflections were measured in this way. Three standard reflections were observed periodically and these observations indicated that no decomposition occurred during the data collection.

The intensity data were corrected for Lorentz-polarization effects and for effects due to absorption. The absorption correction was made using a modified version of OR ABS;²⁸ the maximum and minimum

transmission factors were 0.93 and 0.79 respectively. The estimated error in each intensity was calculated by

$$[\sigma(I)]^2 = [C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2 + (K_R C_R)^2] / A^2$$

where C_T , C_B , C_R , and A are total count, background count, net count, and transmission factor while K_T , K_B , and K_R are estimated non-statistical errors in C_T , C_B , and C_R . K_T and K_B were assigned values of .05 and K_R .03. The equivalent values of the intensities were then averaged. The estimated standard deviations in each structure factor was calculated from the mean deviation in intensity by the method of finite differences.⁸ The reciprocals of the structure factor variances were used as weights in the least squares refinement. The results reported are based on 1855 observed reflections which had an intensity greater than $3\sigma(I)$, a criteria that appeared valid from measurements of intensities of symmetry extinct reflections.

Solution of the Structure

From the symmetry of the monoclinic space group $P_{21/c}$ and the presence of approximately six molecules of stoichiometry $\text{CuL}_2\text{NCSClO}_4$ per unit cell, two of the six molecules must necessarily possess a center of symmetry, which would be impossible for ordered $\text{CuL}_2\text{NCSClO}_4$, assuming a monomeric species with a copper at a $\bar{1}$ site. Thus, the stoichiometry was immediately suspect. A copper atom was assumed at 0.5, 0, 0, 0.5, and the other copper atom in the asymmetric unit was

readily located from a sharpened Patterson map;²¹ all other nonhydrogen atoms were subsequently found by successive structure factor and electron density map calculations. With all atoms isotropic, the structure refined to 16.4%. At this point a difference electron density map indicated appreciable anisotropic motion, especially of the copper, chlorine, and sulfur atoms. Refinement with these heavy atoms anisotropic produced an R factor of 14.0% and weighted R factor $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 14.4%.¹³ A difference electron density map at this stage showed no significant peaks, indicating all nonhydrogen atoms had been located. Hydrogen positions for the aromatic rings were calculated assuming a benzoid structure with a C-H bond distance of 1.07 Å. Each hydrogen atom was assigned the isotropic temperature factor of the carbon to which it was attached. The scattering factors used were those of Hansen *et al.*¹¹ with copper, chlorine, and sulfur modified for the real and imaginary parts of anomalous dispersion.¹² The final values of the observed and calculated structure factors ($\times 10$) are listed in Figure 9. The final positional and thermal parameters for the nonhydrogen atoms are given in Tables XI and XII. The calculated hydrogen positions are given in Table XIII. Bond distances and angles about the copper(II) ions are given in Table XIV, along with the average distances for chemically equivalent bond lengths in the individual ligands. Results for least-squares planes calculations involving the metal ions are provided in Table XV.

Figure 9. Observed and calculated structure factors ($\times 10$) for $\text{CuL}_2(\text{NCS})_2\text{CuL}_2\text{NCSClO}_4$ (L = 2,2'-bipyridylamine)

L = 0				L = 1				L = 2				L = 3				L = 4			
M	K	FO	FC	M	K	FO	FC	M	K	FO	FC	M	K	FO	FC	M	K	FO	FC
1	0	3211	3176	8	9	449	460	10	4	244	310	5	11	575	597	7	5	503	754
2	0	2450-2239		9	9	312	-126	10	4	218	144	7	11	794	739	11	5	303	347
4	0	858	-684	0	10	724	948	-11	5	355	166	-6	12	237	131	-4	6	602	709
5	0	726	-739	1	13	461	-385	-6	12	238	131	-3	6	255	-302	-1	6	835	891
6	0	293	-238	2	10	419	-282	-6	12	239	131	-2	6	289	-409	8	1	191	-142
7	0	242	-114	3	13	471	-164	-6	12	240	131	-1	6	211	287	9	1	262	198
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-7	9	269	-345	-2	7	255	-276	7	4	591	-746	3	5	503	419	-5	6	749	-233	-5	4	381	-362
-2	9	272	317	-2	7	345	-276	3	4	422	-373	4	5	654	-597	-3	6	485	-431	-4	4	250	-239
-1	9	606	533	0	7	421	-428	4	4	282	-418	5	5	228	103	-2	6	531	640	-3	4	597	-677
0	9	494	421	1	7	284	-187	-9	5	249	-156	6	5	575	-755	0	6	617	561	-1	4	1091	-1111
1	9	818	781	2	7	459	-557	-6	5	210	-158	7	5	348	268	1	6	321	259	-7	5	373	332
4	9	272	-271	3	7	492	-381	-5	5	776	-726	-7	6	409	-369	2	6	361	359	-1	5	362	-286
-7	10	279	-245	-4	8	251	-129	-4	5	356	-256	-5	6	310	-414	-3	7	496	465	0	5	298	-147
-1	10	256	-295	-3	8	207	157	-3	5	368	-467	-3	6	194	-205	-2	7	390	412	-6	6	329	200
0	10	205	137	-1	9	272	164	0	5	204	133	-2	6	292	285	-1	7	740	673	-4	6	354	252
1	10	589	-541	0	9	231	229	3	5	698	661	-1	6	647	622	0	7	427	310	-5	7	392	374
2	10	252	161	7	9	230	-215	4	5	334	413	0	6	871	819	1	7	281	-382	0	7	279	-306
4	10	512	431	-7	9	294	249	5	5	611	621	1	6	992	966	3	7	330	-217	-1	8	339	252
-3	11	318	376	-5	9	398	481	-6	6	320	366	2	6	355	293	4	7	216	-221	-1	8	742	318
-2	11	270	-133	-4	9	261	-136	-5	6	219	-206	3	6	331	202	-5	8	466	-451	0	9	306	210
-1	11	430	337	-3	9	306	222	-4	6	192	197	4	6	226	-125	-3	8	420	-318				
1	11	535	414	-2	9	270	-267	-3	6	405	-350	6	6	432	-613	1	8	254	144				
3	11	298	155	-1	7	201	118	-2	6	314	295	7	6	313	-170	3	8	448	536	H	K	FO	FC
-3	12	469	-454	0	9	472	-467	-1	6	655	-659	-5	7	231	-309	4	8	452	613	-6	1	252	162
-1	12	270	-346	-3	10	683	544	0	6	824	803	-3	7	389	-410	-3	9	434	-512	-5	1	347	322
2	12	285	354	-2	10	315	411	1	6	413	-524	-2	7	336	-472	-2	9	572	-594	-3	1	320	255
				-1	13	370	376	2	6	629	669	0	7	520	-414	-1	9	792	-888	-2	1	399	-343
				0	13	280	173	3	6	510	-404	1	7	272	323	2	9	404	304	0	1	485	-414
				2	10	257	-149	4	6	265	289	3	7	321	417	1	10	346	-370	-6	2	264	168
				4	10	324	-232	5	6	369	-328	5	7	618	637					-2	2	245	225
				-4	11	282	-163	-5	7	215	-144	7	7	347	465					-1	7	279	269
				0	11	219	-240	-6	7	283	-306	-7	8	295	-136					0	2	613	679
				-4	1	421	405	-2	7	350	-388	-6	8	245	-136	-9	1	410	-391	-6	3	266	-281
				-3	1	561	479	2	7	389	319	-4	9	222	178	-6	1	543	-492	-4	3	417	-349
				-2	1	261	-175	1	7	338	343	-1	8	372	-323	-3	1	719	701	-3	3	417	-354
				-1	1	319	-265	4	7	246	151	1	8	265	-205	-2	1	549	474	-2	3	383	-496
				0	1	1518	-1618	5	7	299	-267	2	8	439	-464	-1	1	545	649	-1	3	448	479
				1	1	508	539	-5	8	293	-271	-5	9	264	-257	0	1	485	406	0	3	265	212
				2	1	697	-607	-3	8	686	-614	-5	9	288	-228	1	1	329	418	-6	4	225	-144
				3	1	915	871	-1	8	689	-585	-4	9	309	-374	3	1	260	172	0	4	326	272
				4	1	440	-422	0	8	417	248	9	9	498	-451	4	1	201	-191	-6	5	285	-151
				5	1	381	395	1	8	697	-635	5	9	474	557	-7	2	302	-229	-4	5	219	-194
				6	1	238	-284	-8	9	492	-418	-1	10	451	-418	-6	2	441	-386	-2	5	236	-238
				7	1	435	437	-7	9	595	579	4	8	447	477	-2	3	340	-411	-1	5	588	608
				10	1	293	281	-5	9	419	459	6	8	598	601	1	10	454	-481	-4	5	465	-672
				-10	2	269	-152	-3	9	816	-920	7	9	259	272	1	11	405	364	-2	2	313	-460
				-5	2	446	496	-2	10	1178	-1052	-5	9	300	470					0	2	272	-325
				-3	2	470	378	-1	9	1406	-1313	-4	9	518	561	-7	3	330	246	-1	6	464	-537
				-2	2	1541	1548	1	0	673	-561	-3	9	389	460	-5	3	309	321	-1	8	275	138
				0	2	967	849	2	0	692	620	1	9	317	-417								
				1	2	665	-698	3	0	452	308	3	9	525	-512								
				3	2	200	-90	4	9	788	791	5	9	393	-358								
				4	2	248	-97	5	0	285	-297	-3	10	218	-292								
				5	2	551	-596	6	0	349	729	-1	10	446	-471								
				6	2	855	-972	7	0	325	225	0	10	435	385								
				7	2	443	-517	8	9	649	738	2	13	350	399								
				8	2	604	-693	9	0	408	359	4	10	416	392								
				9	2	248	-348	-8	1	362	383												
				10	2	272	-151	-7	1	252	166												
				-10	3	260	-327	-6	1	352	456												
				-6	3	355	-422	-4	1	206	-115												
				-5	3	256	-333	-3	1	421	468												
				-4	3	808	-860	-2	1	507	-425												
				-3	3	285	-323	-1	1	456	375												
				-2	3	688	-546	0	1	350	426												
				-1	3	574	437	1	1	736	860												
				0	3	337	327	3	1	496	-507												
				1	3	980	784	4	1	705	-787												
				4	3	251	-257	5	1	796	-803												
				6	3	368	-352	6	1	216	-186												
				7	3	596	684	7	1	218	207												
				8	3	367	-361	8	1	251	271												
				-6	4	275	-234	-9	2	280	-156												
				-5	4	358	-322	-7	2	208	-156												
				-3	4	226	-338	-3	2	327													

Table XI. Final atomic coordinates and isotropic thermal parameters with standard deviations in parentheses^a

Atom	x	y	z	B(Å ²)
Cu(1)	.50 ^{*b}	.00 [*]	.50 [*]	----- ^c
Cu(2)	.9406(3)	.3700(2)	.3447(2)	-----
Cl	.4584(7)	.4301(6)	.3485(5)	-----
S(1)	.8573(12)	.1409(11)	.4997(7)	-----
S(2)	.8698(8)	.6889(6)	.3319(4)	-----
O(1)	.5382(21)	.3669(19)	.3527(13)	7.4(6)
O(2)	.3671(21)	.3886(17)	.3698(12)	7.0(6)
O(3)	.4501(26)	.4637(22)	.2803(18)	11.4(9)
O(4)	.4789(25)	.5075(24)	.3978(16)	11.0(9)
N(1)	.4349(18)	.0408(16)	.4048(11)	3.4(5)
N(2)	.4740(18)	.1958(15)	.4288(12)	3.3(5)
N(3)	.4504(17)	.1234(15)	.5346(11)	3.0(5)
N(4)	.6707(22)	.0663(19)	.4671(14)	6.0(7)
N(5)	.0271(16)	.3774(14)	.2709(10)	2.3(4)
N(6)	.8857(17)	.3553(15)	.1793(11)	2.8(5)
N(7)	.8289(17)	.2879(14)	.2821(12)	3.1(5)
N(8)	.8721(19)	.3834(16)	.4320(12)	3.9(6)

^aEstimated standard deviations are given for the least significant figures.

^bAsterisk (*) indicates position fixed by symmetry.

^cAnisotropic temperature factors for Cu, Cl, and S atoms are given in Table XII.

Table XI (continued)

Atom	x	y	z	B($\text{\AA}^2$)
N(9)	.0308(19)	.3410(17)	.5011(12)	3.8(6)
N(10)	.0384(20)	.2710(18)	.3895(13)	4.8(6)
N(11)	.8953(19)	.5001(19)	.3195(12)	4.4(6)
C(1)	.3859(25)	-.0313(20)	.3628(15)	4.2(7)
C(2)	.3501(25)	-.0038(24)	.2933(17)	4.9(8)
C(3)	.3668(23)	.0889(20)	.2723(15)	3.5(7)
C(4)	.4124(22)	.1535(18)	.3170(15)	3.2(7)
C(5)	.4319(20)	.1291(19)	.3897(14)	2.7(6)
C(6)	.4559(19)	.1989(18)	.4984(14)	2.3(6)
C(7)	.4410(24)	.2888(21)	.5340(17)	4.1(8)
C(8)	.4051(27)	.2961(24)	.6002(19)	5.9(9)
C(9)	.3986(26)	.2108(22)	.6308(16)	4.8(8)
C(10)	.4169(22)	.1257(22)	.6017(15)	3.9(7)
C(11)	.7538(17)	.1151(14)	.4875(11)	0.10(6)
C(12)	.1271(30)	.4085(23)	.2778(18)	5.5(9)
C(13)	.1924(31)	.4375(26)	.2292(21)	6.7(10)
C(14)	.1493(26)	.4571(22)	.1578(17)	4.8(8)
C(15)	.0398(27)	.4270(21)	.1462(17)	4.4(8)
C(16)	.9829(29)	.3851(23)	.1971(18)	5.7(9)
C(17)	.8292(25)	.2986(21)	.2098(17)	4.1(7)
C(18)	.7475(28)	.2390(23)	.1707(17)	5.3(8)

Table XI (continued)

Atom	x	y	z	B($\text{\AA}^2$)
C(19)	.6806(25)	.1892(21)	.2083(17)	4.2(7)
C(20)	.6877(31)	.1737(26)	.2793(21)	6.8(10)
C(21)	.7613(25)	.2334(22)	.3157(16)	4.2(8)
C(22)	.7694(25)	.4197(20)	.4312(16)	4.0(7)
C(23)	.7290(26)	.4475(23)	.4884(18)	5.1(8)
C(24)	.7825(27)	.4436(22)	.5450(17)	5.0(8)
C(25)	.8854(24)	.4096(20)	.5550(15)	3.8(7)
C(26)	.9351(23)	.3778(19)	.4963(15)	3.3(7)
C(27)	.0654(24)	.2759(21)	.4600(16)	3.9(7)
C(28)	.1407(23)	.2056(19)	.4890(15)	3.4(7)
C(29)	.1699(27)	.1381(24)	.4451(18)	5.6(9)
C(30)	.1364(25)	.1316(23)	.3724(17)	5.0(8)
C(31)	.0641(23)	.2018(21)	.3501(15)	3.6(7)
C(32)	.8791(27)	.5772(25)	.3249(17)	4.9(8)

Table XII. Anisotropic temperature factors^a with standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	97(5)	21(2)	13(2)	8(3)	-19(2)	-1(2)
Cu(2)	64(3)	27(2)	17(1)	2(3)	-9(1)	1(1)
Cl	58(7)	58(5)	41(4)	19(6)	-5(4)	14(4)
S(1)	202(18)	135(12)	67(6)	-70(12)	34(8)	29(7)
S(2)	140(11)	77(5)	22(3)	4(6)	-26(5)	3(3)

^aThe β_{ij} and their standard errors are $\times 10^4$. The β_{ij} are defined by:

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

Table XIII. Calculated hydrogen atom positions^a

Atom ^b	x	y	z
H(1)	.377	-.099	.381
H(2)	.312	-.051	.259
H(3)	.344	.109	.221
H(4)	.433	.219	.299
H(7)	.458	.350	.508
H(8)	.386	.359	.624
H(9)	.377	.210	.682
H(10)	.406	.065	.629
H(12)	.045	.412	.269
H(13)	.273	.446	.243
H(14)	.192	.489	.120
H(15)	.002	.438	.097
H(18)	.743	.236	.116
H(19)	.616	.159	.180
H(20)	.644	.123	.304
H(21)	.764	.235	.370
H(22)	.724	.425	.384
H(23)	.652	.474	.484
H(24)	.748	.464	.600
H(25)	.929	.407	.603
H(28)	.170	.208	.541
H(29)	.221	.089	.466
H(30)	.163	.080	.339
H(31)	.029	.198	.299

^aHydrogen positions were calculated assuming a benzoid structure and a bond length of 1.07 Å.

^bThe atom number is that of the carbon atom to which the hydrogen is attached.

Table XIV. Selected interatomic distances and angles for $\text{CuL}_2(\text{NCS})_2$
 $\text{CuL}_2\text{NCSClO}_4$

Atoms	Distance (Å)	Atoms	Angle (°) e. s. d. = 2.0°
Cu(1)-N(3)	2.02(2)	N(3)-Cu(1)-N(1)	94
Cu(1)-N(1)	2.05(2)	N(3)-Cu(1)-N(1)'	85
Cu(1)-N(4)	2.49(3)	N(3)-Cu(1)-N(4)	87
Cu(2)-N(5)	1.86(2)	N(3)-Cu(1)-N(4)'	92
Cu(2)-N(8)	1.96(2)	N(1)-Cu(1)-N(4)	91
Cu(2)-N(11)	2.02(2)	N(1)-Cu(1)-N(4)'	88
Cu(2)-N(10)	2.05(2)	N(5)-Cu(2)-N(8)	166
Cu(2)-N(7)	2.16(2)	N(5)-Cu(2)-N(11)	86
S(1)-C(11)	1.37(3)	N(5)-Cu(2)-N(10)	89
S(2)-C(32)	1.63(3)	N(5)-Cu(1)-N(7)	90
C(11)-N(4)	1.32(4)	N(8)-Cu(2)-N(11)	88
C(32)-N(11)	1.14(4)	N(8)-Cu(2)-N(10)	89
Cl-O(1)	1.37(3)	N(8)-Cu(2)-N(7)	102
Cl-O(2)	1.39(3)	N(11)-Cu(2)-N(10)	155
Cl-O(3)	1.40(4)	N(11)-Cu(2)-N(7)	102
Cl-O(4)	1.48(3)	N(10)-Cu(2)-N(7)	102

Table XIV (continued)

Mean Distances for Chemically Equivalent Bonds

Ligand 1 [C(1) ... C(10) N(1) ... N(3)]

mean C-C 1.42(3)

mean C-N (pyridyl) 1.36(3)

mean C-N (bridge) 1.35(3)

Ligand 2 [C(12) ... C(21) N(5) ... N(7)]

mean C-C 1.42(4)

mean C-N (pyridyl) 1.41(4)

mean C-N (bridge) 1.30(4)

Ligand 3 [C(22) ... C(31) N(8) ... N(10)]

mean C-C 1.41(4)

mean C-N (pyridyl) 1.39(4)

mean C-N (bridge) 1.33(4)

Table XV. Least squares planes^a

<u>Plane</u>	<u>l</u>	<u>m</u>	<u>n</u>	<u>k</u>
1	.879	.424	-.220	2.94
2	.672	.562	.481	-14.4

Deviations from Plane

<u>Atom</u>	<u>Plane 1</u>	<u>Plane 2</u>
Cu(1)	0.00	
Cu(2)		-.33 ^{*c}
N(1)	0.00	
N(3)	0.00	
N(1') ^b	0.00	
N(5)		-.10
N(7)		-2.48 [*]
N(8)		-.10
N(10)		.10
N(11)		.10

^aThe planes $lX' + mY' + nZ' + k = 0$ are referred to orthogonal axes. The transformation from fractional cell coordinates (x, y, z) is $X' = ax + cz(\cos\beta)$, $Y' = yb$, $Z' = zv/ab$.

^bPrimed atoms related to unprimed atoms by the symmetry operation $1-x, -y, 1-z$.

^cStarred atoms were not included in least squares plane.

Description of the Structure and Discussion

The crystal structure of the co-crystallized complexes di-isothiocyanatobis (2,2'bipyridylamine) copper(II) and isothiocyanatobis (2,2'bipyridylamine) copper(II) perchlorate consists of two monomeric molecules in the asymmetric unit. The first species $\text{CuL}_2(\text{NCS})_2$ utilizes a centrosymmetric special position of the space group, while $\text{CuL}_2\text{NCSClO}_4$ is in a four-fold general position. The geometry of $\text{CuL}_2(\text{NCS})_2$ and CuL_2NCS^+ are shown in Figures 10 and 11, respectively, while Figure 12 is a view of the formula unit.

In $\text{CuL}_2(\text{NCS})_2$, the copper(II) ion is in a tetragonally distorted octahedral environment with $\bar{4}$ symmetry. Hence, the 2,2'bipyridylamine ligand coordinates in a bidentate fashion with Cu-N bond lengths of 2.02 and 2.05 Å, while the isothiocyanate groups are trans to each other with a Cu-N distance of 2.50 Å. N(1), N(3), N(1)', N(3)' are coplanar with the copper atom within standard deviations (see Table XV and Figure 9). There is very little angular distortion from true octahedral geometry, with the elongated isothiocyanate nitrogen forming nearly 90° N-Cu-N bond angles with the nitrogens of the bidentate ligand. The intraligand N-Cu-N angle is 85°, reflecting the geometric requirements of the ligand.

In the five coordinate species the copper is bound to the pyridyl nitrogen atoms of two bidentate ligands and to the isothiocyanate group in a configuration that is best described as square pyramidal. The atoms in the base consist of N(5), N(8), N(10), N(11) with N(7) at the apex. The copper nitrogen bond distances in the base are normal

Figure 10. A view displaying the tetragonally distorted geometry of the di-isothiocyanatobis (2,2'-bipyridylamine) copper(II) moiety

Figure 11. A view of the isothiocyanatobis (2,2'-bipyridylamine) copper(II) ion, displaying the square pyramidal geometry

Figure 12. A formula unit of $\text{CuL}_2(\text{NCS})_2\text{CuL}_2\text{NCSClO}_4$ (L = 2,2'-bipyridylamine)

except Cu(2)-N(5) at 1.86 Å. (Since the crystal was a poor diffractor, there were a large number of small reflections with associated large relative errors. It is likely that this anomalously short distance is due to a systematic effect from this poor diffraction data and therefore should be viewed with skepticism. Such effects can also be seen in other bond distances in the a direction in particular. The overall stereochemistry is well established, however.)⁵ The choice of basal atoms is supported by the near planarity of the four atoms (Table XV) and the bond angles of approximately 90° formed by N(10)-Cu(2)-N(8) (89°), N(8)-Cu(2)-N(11) (89°), N(5)-Cu(2)-N(11) (87°), and N(10)-Cu(2)-N(5) (89°). The copper atom is above the plane of the base by .33 Å and forms a bond of 2.14 Å with N(7); this vector is perpendicular, within experimental error, to the basal plane. This distance is quite typical of the apex distance found in other copper(II) square pyramidal complexes, as is the position of the copper atom above the plane of the base.³

The 2,2'-bipyridylamine ligands of both chromophores are bent considerably about the bridging nitrogen. In the centrosymmetric complex the dihedral angle between the two pyridine rings is 38° and thereby reduces the crowding between the two ligands. The distance between C(10) and C(1') is 2.90 Å while the distance between the associated hydrogen atoms is 2.83 Å. The dihedral angle in this chromophore is identical to the similar angle found in the square planar palladium complex with this ligand.⁶ In the five coordinate species the dihedral angles for ligands 2 and 3 (defined in Table XIV)

are slightly different from ligand I at 25° and 35°, respectively.

In $(\text{CuL}_2\text{I})_2\text{IClO}_4$ ($\text{L} = 2,2'$ bipyridylamine), a five-coordinate trigonal bipyramidal complex, the angles are 38° and 33°, while in the distorted tetrahedral complex, $\text{CuL}_2(\text{ClO}_4)_2$, the ligand is nearly planar with a 9.6° dihedral angle. The six-membered chelate rings in these complexes are quite similar, all showing approximately the same degree of folding in the boat conformation. For ligands 1, 2, and 3 (defined in Table XIV) the copper atom is .77, .68, and .78 Å below the plane defined by the other four atoms, while the nitrogen atoms are .41, .18, and .19 Å below the plane.

The average carbon-carbon bond distance in the ligand is 1.42 Å, while the average C-N distance in the pyridyl ring is 1.39 Å and the average C-N bridging distance is unusually short at 1.34 Å.

The isothiocyanate group bound to Cu(I) forms a Cu-N-C bond angle of 144°, considerably distorted from the normal linear configuration. Smaller angles have been reported, however, for the isothiocyanate group bound to a transition metal, the smallest being 140°. ²⁹ The N-C and C-S distances found in the isothiocyanate group in molecule I do not agree well with accepted literature values. Unusual behavior of the thermal parameters for S(1) and C(11) lead to the conclusion that this group is also effected by the poor data mentioned earlier. The isothiocyanate group in molecule II, however, is quite normal in distances and is more nearly linear with a Cu(2)-N(11)-C(32) bond angle of 161°.

Lancaster has recently pointed out that the infrared spectra for $\text{CuL}_2\text{NCSClO}_4$ is indicative of two crystallographically unique isothiocyanate groups.²⁵ This leads to the speculation that the compound originally reported by McWhinnie may indeed be the same as the mixture in this study.

The observed crystal structure is stabilized by hydrogen bond formation (Table XVI) involving as receptor atoms the sulfur atoms of the isothiocyanate groups in each chromophore and an oxygen atom of the perchlorate group. In each case the linkage is with an amine hydrogen atom. The $\text{N}(2) \dots \text{O}(1)$ distance of 3.08 Å is within that normally found for $\text{N-H} \dots \text{O}$ hydrogen bond formation. Also the bond angles $\text{O}(1)\text{-N}(2)\text{-C}(5)$ (114°) and $\text{O}(1)\text{-N}(2)\text{-C}(6)$ (100°) indicate the near linearity of the linkage. In the crystal structure of the parent uncoordinated ligand, which is also stabilized by hydrogen bonding, the C-N-H bond angle is 114° .

Hydrogen bonding also occurs between $\text{S}(1)$ and $\text{N}(6)$ at a distance of 3.49 Å and bond angles of 117° and 107° for $\text{C}(17)\text{-N}(6)\text{-S}(1)$ and $\text{C}(16)\text{-N}(6)\text{-S}(1)$, respectively. An additional hydrogen bond links the two positive ions, the $\text{S}(2) \dots \text{N}(9)$ distance being 3.44 Å with bond angles of 111° and 113° for $\text{C}(27)\text{-N}(9)\text{-S}(2)$ and $\text{C}(26)\text{-N}(9)\text{-S}(2)$. Crystallization is a commonly used technique for purification and separation of materials. It is unusual to find two such metal complexes co-crystallizing. The hydrogen bonds between the neutral complex and the two ions of compound II may well account for this behavior.

Table XVI. Hydrogen bonds^a in $\text{CuL}_2(\text{NCS})_2\text{CuL}_2\text{NCSClO}_4$

Bond N-H ... Y	Distance (Å) N-Y	Angles ^c (°)
N(2)-H ^b ... O(1)	3.02	114, 110
N(6)-H ... S(1) ^I	3.47	117, 107
N(9)-H ... S(2) ^{II}	3.42	111, 113

^aRoman numerals refer to the following symmetry transformation:
 I: $x, \frac{1}{2}-y, z-\frac{1}{2}$; II: $1-x, 1-y, 1-z$.

^bHydrogen atom positions were not located.

^cAll hydrogen bond linkages are to amine hydrogen atoms. The bond angles referred to are the C-N ... Y for the two carbon atoms bound to the nitrogen. In the parent uncoordinated ligand a hydrogen bond of this type stabilizes the crystal structure and a C-N-H bond angle of 114° was found.

THE STRUCTURE OF 2,2'BIPYRIDYLAMINE

Introduction

The structural study of 2,2'bipyridylamine was undertaken to obtain accurate structural parameters for this moiety since it has been finding wide use as a ligand in transition metal complexes. McWhinnie has recently reviewed this aspect of its ligand chemistry.¹ The compound itself was first reported in 1923 by Wibaut and Dingemans.³⁰ Two crystalline modifications of the compound are known, one melting at 84° and a second melts at 94°. The structure of the low melting polymorph was determined in this study.

Experimental

Crystal Data. --2,2'bipyridylamine, $C_{10}H_9N_3$, $M = 171$ g/m

Orthorhombic, P_{ccn} , $a = 18.416 \pm .005$, $b = 12.294 \pm .005$,
 $c = 7.691 \pm .007$ Å, $V = 1741.3$ Å³, $\rho_c = 1.31$ g/cc, $Z = 8$, $F(000) = 720$ e,
 MoK_{α} ($\lambda = 0.7107$ Å), $\mu = 1.03$ cm⁻¹, M.P. = 84°.

Recrystallization of reagent grade 2,2'bipyridylamine from carbon tetrachloride yielded large colorless crystals of rectangular needle-like habit and well-formed faces. Precession and Weissenberg photographs exhibited mm m Laue symmetry with the following systematic extinctions: $h0\ell$ when $\ell = 2n+1$, $0k\ell$ when $\ell = 2n+1$, and $hk0$ when $h+k = 2n+1$. These absences uniquely determine the space group as P_{ccn} . The unit cell parameters and their standard deviations were determined by a least squares fit to 12 independent reflection angles¹⁹ whose centers were determined by left-right, top-bottom beam splitting on a previously aligned four-circle diffractometer.

For data collection a crystal of dimensions .10 x .25 x .50 mm along the a, b, and c crystal axes respectively was mounted such that the c axis was along the spindle axis of the goniometer. Since crystal decomposition in the atmosphere had previously been noticed, the crystal was housed in a thin-walled Lindemann glass capillary. Data were collected at room temperature (24°C) utilizing an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from Stoe and equipped with encoders (Baldwin Optical) and drive motors. The base was so designed that encoders could be directly connected to the main ω and 2θ shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer and is equipped with a scintillation counter. Two equivalent octants of data were collected within a 2θ sphere of 40° . The θ - 2θ step scan technique, $.01^\circ/\text{step}$ counting for .10 sec/step, was employed with a takeoff angle of 3° . To improve the efficiency of the data collection process, variable-step symmetric-scan ranges were used. The scan varied from 1.12° in 2θ at low two-theta values to 1.72° at large two-theta angles. Stationary-crystal, stationary-counter back-round counts of one-half the time required to scan the peak were taken at the beginning and end of each scan. Before the scan was made each peak was maximized in ω . Also if the reflection did not exceed the background by seven counts or more, which corresponds to approximately three standard deviations in the background for larger values of 2θ , no further measurements were made on the reflection.

As a general check on electronic and crystal stability, the intensities of three standards were remeasured every twenty-five reflections. These standards showed no decrease over the entire period of data collection. A total of 1771 reflections were recorded in the hkl and $\bar{h}k\bar{l}$ octants.

The intensity data were corrected for Lorentz-polarization effects. Because of the small linear absorption coefficient, no absorption correction was made. The minimum and maximum transmission factors were .95 and .99, respectively. The individual values of F_0^2 from the equivalent octants were averaged to yield 809 unique F_0^2 values. The standard deviation in each intensity was estimated from the average total count and background values by

$$[\sigma(I)]^2 = [c_t + c_b + (0.05 c_t)^2 + (0.05 c_b)^2] .$$

Of the 809 unique reflections, 567 had $F_0^2 \geq 3.0 \sigma(I)$. The estimated standard deviation in each structure factor was calculated by the method of finite differences. The reciprocals of the squares of the structure factor variances were used as weights in the least squares refinement.

Solution and Refinement

Normalized structure factors³¹ were calculated preliminary to a direct method structure determination attempt. However, the Wilson plot from which the scale factor and temperature factor were obtained

gave quite a poor fit to a straight line. Subsequent phasing via the Σ -2 relation lead to a chemically satisfying model, but one which would not refine.

At this stage it was noticed that the e_{eo} and e_{oo} parity groups had average values of $|E|^2$ significantly below 1.0. These parity groups were arbitrarily rescaled to 1.0 and the program MULTAN³² was employed to obtain phases for all reflections with E 's greater than 1.0. The E-map computed unambiguously showed the positions of all 13 heavy atoms in the structure. The model originally produced by the Σ -2 application was related to the true structure by a two-fold rotation about the point $x = 1/2$ and $y = 3/4$. With all atoms but the bridging nitrogen input as carbons, four cycles of least squares refinement produced a crystallographic discrepancy factor of 13.2%. The ring nitrogen positions were readily determined by their low temperature factors and by their shorter bond distances. With all atoms isotropic, R was 11.00%, and the weighted R factor, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, was 12.90% for the 567 observed reflections. The scattering factors used for the carbon and nitrogen were those of Hansen et al.¹¹ A difference electron density map at this stage showed that all nonhydrogen atoms had been accounted for, but some anisotropic motion was evident. Three additional cycles of anisotropic refinement of all heavy atoms reduced the discrepancy factor to 9.8% and R_w to 11.3%. A subsequent difference map clearly indicated all nine hydrogen atom positions.

At this stage two reflections, 202 and 220, appeared to be severely effected by extinction and were removed from the refinement. The hydrogen positions were input lowering the agreement factor to 4.1%, however, some of the isotropic thermal parameters went negative. This was attributed to the use of the isolated hydrogen atom scattering factors leading to an undesirable interaction between the thermal parameter and the aspherical electron density distribution for bound hydrogen, as described by Jenson and Sundarlingam.³³ Using the contracted hydrogen atom scattering factor of Stewart, Davidson, and Simpson,³⁴ positive isotropic thermal parameters were derived. With these scattering factors refinement gave a final discrepancy factor of 3.8% was obtained, with $R_w = 4.3\%$ for the 565 observed reflections. At this point two final cycles of least squares were run with all 807 uniquely measured reflections yielding $R = 6.2\%$ and $R_w = 5.3\%$. No appreciable shifts in atom positions occurred. The final value of $[\sum w^2 / (NO - VN)]^{1/2}$ was .7823.

In Table XVII are listed the final positional and thermal parameters of the heavy atoms along with their standard deviations. The refined positional and isotropic thermal parameters and their standard deviations for the hydrogen atoms are given in Table XVIII. Standard deviations given were obtained from the inverse matrix of the final least-squares refinement cycle. A list of all 807 unique recorded and calculated structure factors ($\times 10$) is found in Figure 13. The bond lengths and bond angles with standard deviations are given in Tables XIX and XX and in Figure 14. Significant nonbonded distances

Table XVII. Final heavy atom atomic coordinates and thermal parameters for 2,2'-bipyridylamine^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.4805(2)	0.8697(4)	0.2168(5)	31(2)	85(4)	259(10)	11(2)	-7(3)	1(5)
C(2)	0.4524(2)	0.7692(4)	0.1838(5)	30(2)	94(4)	240(9)	-3(2)	-12(3)	-24(5)
C(3)	0.4955(2)	0.6806(4)	0.2183(5)	43(2)	73(4)	253(10)	-5(2)	-8(3)	-25(5)
C(4)	0.5635(2)	0.6964(3)	0.2846(5)	34(2)	61(3)	249(9)	3(2)	-15(3)	-20(5)
C(5)	0.5876(2)	0.8018(3)	0.3162(4)	22(1)	69(3)	173(8)	6(2)	2(2)	-8(4)
C(6)	0.6912(2)	0.9073(3)	0.4451(4)	26(1)	55(3)	172(7)	0(2)	0(3)	5(4)
C(7)	0.6558(2)	1.0030(3)	0.4934(5)	31(2)	69(3)	218(9)	11(2)	-6(3)	-14(4)
C(8)	0.6964(2)	1.0868(3)	0.5580(5)	39(2)	66(3)	241(9)	10(2)	-6(3)	-15(5)
C(9)	0.7704(2)	1.0761(3)	0.5742(5)	42(2)	66(4)	224(9)	-5(2)	-4(3)	-8(5)
C(10)	0.8007(2)	0.9783(3)	0.5273(5)	28(2)	82(4)	231(9)	-2(2)	-8(3)	2(5)
N(1)	0.5469(2)	0.8888(2)	0.2825(4)	25(1)	75(3)	249(7)	5(1)	-10(2)	-4(3)
N(2)	0.6564(2)	0.8157(3)	0.3834(4)	26(1)	54(3)	257(8)	7(2)	-6(2)	-4(4)
N(3)	0.7630(2)	0.8946(2)	0.4624(4)	26(1)	59(2)	226(7)	1(1)	-4(2)	1(3)

^aStandard deviations of the coordinates are for the least significant figure. The β_{ij} and their standard deviations are $\times 10^4$. The β_{ij} are defined by:

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

Table XVIII. Refined hydrogen atom parameters^a

Atom	x	y	z	B (Å ²)
H(1)	0.454(2)	0.935(3)	0.190(4)	4.5(9)
H(2)	0.403(2)	0.763(3)	0.131(4)	5.1(9)
H(3)	0.479(2)	0.611(3)	0.190(5)	6.4(10)
H(4)	0.594(2)	0.635(3)	0.307(4)	4.0(8)
H(5) ^b	0.681(2)	0.756(3)	0.396(4)	4.1(9)
H(7)	0.605(2)	1.008(2)	0.481(4)	4.0(8)
H(8)	0.668(2)	1.156(3)	0.589(5)	6.5(10)
H(9)	0.800(2)	1.135(3)	0.622(5)	6.3(10)
H(10)	0.850(2)	0.967(3)	0.541(4)	3.7(8)

^aThe number of the hydrogen atom is that of the carbon to which it is attached.

^bH(5) is the amine hydrogen attached to N(2).

Figure 13. Observed and calculated structure factors ($\times 10$) for
2,2'-bipyridylamine

Table XIX. Interatomic distances and angles in 2,2'-bipyridylamine

A. Distances (Å)			
C(1)-C(2)	1.362(5)	C(9)-C(10)	1.374(5)
C(2)-C(3)	1.374(5)	C(1)-N(1)	1.345(4)
C(3)-C(4)	1.367(5)	C(5)-N(1)	1.332(4)
C(4)-C(5)	1.391(4)	C(5)-N(2)	1.379(4)
C(6)-C(7)	1.395(5)	C(6)-N(2)	1.380(4)
C(7)-C(8)	1.367(5)	C(6)-N(3)	1.338(4)
C(8)-C(9)	1.375(5)	C(10)-N(3)	1.337(4)
B. Angles (°) e.s.d. = 0.4°			
N(1)-C(1)-C(2)	125.1	N(3)-C(10)-C(9)	124.0
C(1)-C(2)-C(3)	117.6	C(10)-C(9)-C(8)	117.6
C(2)-C(3)-C(4)	119.2	C(9)-C(8)-C(7)	120.3
C(3)-C(4)-C(5)	119.4	C(8)-C(7)-C(6)	118.4
C(4)-C(5)-N(1)	122.3	C(7)-C(6)-N(3)	122.3
C(5)-N(1)-C(1)	116.4	C(6)-N(3)-C(10)	117.5
N(1)-C(5)-N(2)	119.4	N(3)-C(6)-N(2)	113.5
N(2)-C(5)-C(4)	118.3	N(2)-C(6)-C(7)	124.2
C(5)-N(2)-C(6)	131.1		

Table XX. Interatomic distances and angles involving hydrogen atoms

A. Distances (Å) e.s.d. = .03 Å			
C(1)-H(1)	.96	C(10)-H(10)	.92
C(2)-H(2)	.99	C(9)-H(9)	.98
C(3)-H(3)	.94	C(8)-H(8)	1.03
C(4)-H(4)	.95	C(7)-H(7)	.94
N(2)-H(5)	.87	H(5) ... N(3) ^a	2.18

B. Angles e.s.d. = 2.0°			
H(1)-C(1)-N(1)	113	H(10)-C(10)-N(3)	116
H(1)-C(1)-C(2)	122	H(10)-C(10)-C(9)	120
H(2)-C(2)-C(1)	120	H(9)-C(9)-C(8)	121
H(2)-C(2)-C(3)	123	H(9)-C(9)-C(10)	121
H(3)-C(3)-C(2)	119	H(8)-C(8)-C(7)	116
H(3)-C(3)-C(4)	121	H(8)-C(8)-C(9)	124
H(4)-C(4)-C(5)	121	H(7)-C(7)-C(6)	120
H(4)-C(4)-C(3)	119	H(7)-C(7)-C(8)	122
H(5)-N(2)-C(5)	114	H(5)-N(2)-C(6)	114

^aHydrogen bond. N(3)' is related to N(3) by the symmetry operation $3/2 - x, 3/2 - y, z$.

Figure 14. A dimeric unit of 2,2'-bipyridylamine displaying the two-fold symmetry

are listed in Table XXI, with least squares plane information provided in Table XXII.

Description of the Structure and Discussion

The low melting polymorph of 2,2'-bipyridylamine contains pairs of molecules hydrogen bonded to one another, the dimeric unit possessing two-fold crystallographic symmetry. Within the molecule the carbon-carbon bonds adjacent to the bridgehead nitrogen are found to be significantly different in length (1.395(5) Å) from the remaining carbon-carbon distances (1.369(5) Å). The latter are somewhat shorter than pyridine C-C distances previously reported.³⁵ The carbon-nitrogen distances in the pyridine rings average 1.338(4) Å with no significant deviations and are virtually identical to the 1.340 Å C-N distance reported for pyridine.³⁵ The two bridging C-N bond distances are identical at 1.380 Å. The bond angles within the pyridine rings vary between 117.6° (C(1) - C(2) - C(3), C(8) - C(9) - C(10)) and 125.1° (N(1) - C(1) - C(2)). The bond angles about chemically equivalent atoms in the two pyridine rings are equal within standard deviations. Bond angles involving the bridging nitrogen are reasonable in the light of repulsive and attractive forces present. The C(6) - N(2) - C(5) angle of 131.1° reflects the nonbonded repulsions between H(7) and N(1) at 2.38 Å. The hydrogen bonding between the moieties probably accounts for the 113.5° angle found for the N(3) - C(6) - N(2).

The carbon-hydrogen bond distances range from .92 Å (C(10) - H(10)) to 1.03 Å (C(8) - H(8)), the average being .96 Å. The N-H distance is

Table XXI. Nonbonded interatomic distances (Å) for 2,2'-bipyridylamine^a

N(1) ... H(7)	2.38	C(10) ... C(7 ^{VI})	3.69
H(1) ... H(7 ^{II})	2.84	C(9) ... C(6 ^{VI})	3.60
H(2) ... H(8 ^{III})	2.52	N(3) ... C(6 ^{VI})	3.81
H(3) ... H(7 ^{III})	2.39	N(2) ... C(4 ^V)	3.53
H(9) ... H(8 ^{IV})	2.64	N(1) ... H(10 ^{VII})	2.83
C(3) ... C(5 ^V)	3.53	N(2) ... C(10 ^{VII})	3.48
C(3) ... N(1 ^V)	3.59		
C(4) ... N(2 ^V)	3.53		
C(10) ... C(6 ^{VI})	3.33		

^aRoman numerals denote the following symmetry transformations:
 I = $3/2 - x, 3/2 - y, z$; II = $1 - x, 2 - y, 1 - z$; III = $-1/2 + x, 1 - y, 1/2 - z$; IV = $3/2 - x, 5/2 - y, z$; V = $x, 3/2 - y, 1/2 + z$; VI = $3/2 - x, y, 1/2 + z$; VII = $3/2 - x, y, 1/2 + z$.

Table XXII. Least squares planes^a for 2,2'-bipyridylamine

	<u>l</u>	<u>m</u>	<u>n</u>	<u>k</u>
Plane 1	-0.373	-0.041	.927	2.19
Plane 2	-0.129	-0.354	.926	2.42

Deviations from Plane

Plane 1		Plane 2	
Atom	Deviation	Atom	Deviation
C(1)	-.003	C(6)	-.008
C(2)	.005	C(7)	.005
C(3)	.000	C(8)	.004
C(4)	-.003	C(9)	-.011
C(5)	.004	C(10)	.008
N(1)	-.001	N(3)	.000
H(1)	-.05	H(7)	.014
H(2)	-.03	H(8)	-.013
H(3)	-.05	H(9)	.007
H(4)	-.02	H(10)	.034

^aThe planes $lX' + mY' + nZ' + k = 0$ are referred to orthogonal axes. The transformation from fractional cell coordinates (x,y,z) is $X' = xa$, $Y' = ya$, and $Z' = zc$.

.87 Å with H-N-C bond angles of 114° (Table XX).

The rings in the molecule are approximately parallel to the ab plane. As expected, the largest component of anisotropic thermal motion of the heavier atoms is in a direction perpendicular to this plane, with approximately equal root mean square deviations in this direction for all the heavy atoms. The hydrogen isotropic thermal parameters range from 3.7 Å² (H(10)) to 6.5 Å² (H(8)).

The pyridine ring containing N(1) is strictly planar with a maximum deviation of .004 Å from the mean plane, while in the second ring C(9) is displaced by .011 Å from the mean plane, a deviation of borderline significance.

Steric hindrance within the ligand is relieved by a twist of the two rings giving rise to a 23° dihedral angle between them (Figure 15).

The hydrogen bond joining the two molecules is nearly linear with a N(3') ... H(5) - N(2) angle of 172°. The distance between the hydrogen and receptor atom is 2.18 Å while the N(3') ... N(2) distance is 3.02 Å. In spite of the short distance between N(1) and H(7), 2.38 Å, it is unlikely that there is an appreciable linkage between these atoms due to the unfavorable N(1) - H(7) - C(7) angle of 117°.

The crystallographic two-fold axes at $x = 1/4$, $y = 1/4$, and $x = 3/4$, $y = 3/4$ are those running through the center of the dimeric units and these units are layered approximately perpendicular to the z direction (Figure 15). The distance between these layers is nearly 3.7 Å, a value typical of layered aromatic structures. Distances between dimeric units in the same layer approximate those

Figure 15. A stereographic view of the unit cell of 2,2'-bipyridylamine. The origin is in the lower left corner with x up, y across, and z into the page

values expected for Van der Waal's contacts, the shortest being 2.39 Å between H(3) and H(7). All short intermolecular contacts are listed in Table XXI.

It is interesting to speculate on the structural changes that may occur in the transformation of the low melting form to the high melting form of 2,2'-bipyridylamine. If the ring containing N(1) is rotated about the N(2) - C(5) bond to attempt to bring N(1) and H(10) into proximity, the distance between H(4) and H(7) would be reduced to approximately 1.6 Å, making this an unacceptable configuration. If the dimeric units remain in the high melting form, only C-H ... N type hydrogen bonds could be formed. It seems likely therefore that the high melting form undergoes a significant change in structure relative to the low melting form.

With the structural data presently available for transition metal complexes with 2,2'-bipyridylamine, it is not possible to make a meaningful comparison between the coordinated and free ligand. It is hoped that future structure determinations (X-ray and/or neutron) of metal complexes with this ligand will provide structural parameters with errors comparable to those in the present study.

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APPENDIX A: DIRECT PHASE DETERMINATION
BY USE OF LINEAR PROGRAMMING

Introduction

Use of linear equations to directly determine the phases of structure factors for centrosymmetric crystallographic problems was first discussed by Hoppe³⁶ and shortly after by Main and Woolfson.³⁷ In both cases relations were established in reciprocal space making use of null points in the Patterson function. Both methods involve the convolution³⁸ of the electron density function with a function representing the null points in the Patterson; however, the manner in which the null points are used is quite different as are the resulting equations.³⁹ Solution of these linear equations employed standard least squares techniques. However, such techniques can, and often do provide results that are physically unreasonable.

In the present work linear equations are set up in real space, that is, employing directly the Fourier expansion of the electron density function, and use is made of null points in the Patterson or symmetry map.⁴⁰⁻⁴⁴ The linear equations are solved, however, by linear programming algorithms which allow the solutions to be constrained to physically reasonable values.

During the time this work was being performed two papers appeared in which linear programming techniques were used in the solution of the phase problem. The first paper, by Dakin,⁴⁵ employs equations quite different from the present work, while the recent paper by Lesk⁴⁶ is similar but not identical to the present approach.

An outline of the mathematical formulation will be presented as well as some preliminary results obtained in a test of the method on a known structure.

Theory

The following discussion will be for a one-dimensional case but can be readily generalized to three dimensions.

The Fourier expansion of the electron density for a centrosymmetric crystal structure is given by:

$$\rho(x) = \frac{1}{L} (F_0 + 2 \sum_{h=1}^{\infty} |F_h| S_h \cos 2\pi hx) \quad (A1)$$

where $\rho(x)$ is the electron density at point x , L is the length of the unit cell (the volume would be used in three dimensions), F_0 is the number of electrons in the unit cell, $|F_h|$ is the magnitude of the structure factor and S_h is the sign of the structure factor. The magnitude of the structure factor is obtainable from experiment, but the signs are not. In practice the number of terms in the infinite Fourier series is limited by the experimental availability of structure factors and is further restricted by the number that can be conveniently handled in the solution of the problem. To reduce the errors associated with such truncation, use is made of an artificial temperature factor which effects the magnitude of the structure factor but not its phase. By choosing a temperature factor that decreases the resolution of the electron density function to a given value, e.g., 2.0 Å, it is only necessary to use data that significantly contributes to the 2.0 Å

structure within the desired error limitations. From the null points in the Patterson or symmetry map, it is possible to derive positions in space where the electron density is effectively zero, i.e., $\rho(x) \approx 0$. The number of such points is usually quite large and each point results in an equation. These equations are in a form that can be readily solved by linear programming techniques.

The algorithms and principles of linear programming are discussed in many textbooks⁴⁷ and package programs are available for solving problems of this type;⁴⁸ therefore only a brief statement of the linear programming technique will be given here. To use the linear programming method, one must have a mathematically expressible objective function, a set of linear constraints, and a lower bound of zero on the solutions (the non-negativity constraint). In general the problem has more variables than equations, as explained below, and the variables are adjusted in an iterative fashion to satisfy the linear constraints while simultaneously maximizing or minimizing the objective function. In linear programming the equations approximating equalities for the null points in space are allowed to vary from an exact equality in order to maintain the desired constraints. To accomplish this extra variables, known as slack variables, are added to each equation. The solution to this problem must lie within the specified bounds for physical reality while simultaneously reducing the residuals in the linear constraints to a minimum. The choice of objective function assures the minimizations of the residuals.

As an example, assume n null points in electron density space, j structure factors suitably chosen and modified to reduce truncation error, and k structure factors whose phases have previously been determined. In general, three structure factors may be assigned signs to fix the origin, or some structure factors might have been determined in a previous run at lower resolution. If some information regarding an atom position is available (e.g., a heavy atom position determined from the Patterson, but of insufficient size to phase the structure), this information may also be included. Substitution of $(x_h - 1)$ for S_h is made in (1), to satisfy the non-negativity constraint, and the equation is transformed to place all known quantities on the right-hand side, yielding

$$2 \sum_h x_h |F_h| \cos 2\pi h x \cong (2 \sum_h |F_h| \cos 2\pi h x - \sum_k F_k \cos 2\pi k x - F_0). \quad (A2)$$

Three types of linear constraints are now available: n null point equations similar to (2), j constraints bounding the solutions, and possibly a constraint accounting for an atom position that is known. The problem to be solved by the algorithm appears as follows:

$$2 \sum_h x_h |F_h| \cos 2\pi h x + \epsilon_i - \epsilon_i = 2 \sum_h |F_h| \cos 2\pi h x - \sum_k F_k \cos 2\pi k x - F_0, \quad (A3)$$

$$x_h \leq 2.0, \quad (A4)$$

$$2 \sum_h |F_h| X_h \cos 2\pi h x + \epsilon_m - \epsilon'_m = C + R \quad (A5)$$

where R is the right-hand side of equation (3) and C is the numerical value expected for the electron density of the known atom at the particular degree of resolution, a quantity determined by trial. The epsilons are the slack variables mentioned earlier, each equation containing two such variables to account for the non-negativity constraint. It is the sum of these slack variables that are minimized in the objective function.

The problem in this form is readily solved by the IBM Mathematical Programming System.⁴⁸ The solutions consist of values of X_h between zero and two (signs between +1 and -1) and values of the slack variables indicating the errors in the equality approximations for each null point. Only values of X_h corresponding to the integer positive or negative sign are used for definite phase assignment.

Experimental

Although the results reported below do not show conclusive evidence for the effectiveness of the method, it does show the potential of the technique. The structure used for a test case was $(\text{CuL}_2\text{I})_2\text{IClO}_4$ where $L = 2,2'$ bipyridylamine, space group P_{21}/c with 248 atoms in the unit cell. With 59 reflections, 72 null points, one peak position, and a temperature factor resolution of $2.0 \text{ \AA}$, the linear programming method yielded integer values of X_h (zero or two) for 34 reflections, of which 32 were correct. From these results it was possible by a

phase refinement procedure, to obtain the correct signs of all the input reflections and subsequently solve the structure. The time of solution for this test case, containing 136 rows, 339 variables, and converging after 442 iterations, was 2.21 minutes c.p.u. time, using 96 K bytes of storage on the IBM 360/65 computer.

Discussion

While the results obtained are not conclusive, the general approach of the problem seems promising. The primary advantage of the method outlined is that the structure can be solved in various degrees of resolution, keeping the amount of data to a manageable quantity. This is particularly important for large biological structures. In addition, the method allows structural information available from any other approach to be built into the phase determining process, i.e., the position of the heavy atom in the typical protein.

Future work should include extensive testing of the method with particular emphasis on formulation of a more powerful objective function, as the constraints placed on the variables seem quite adequate with most of the solutions clustering at the integer values of zero and two. An objective function similar to the equation derived by Main and Woolfson³⁷ has been examined, in which the electron density is convoluted with a symmetry map function, the result being an objective function that is minimized containing the known coefficients of the Fourier expansion of the symmetry map function and the magnitudes of the structure factors. The results obtained using this objective

function were, however, less satisfactory than those obtained using the minimization of the residuals. Unfortunately, the type of objective function having potentially the greatest power, such as the maximization of the cube of the electron density function,⁴⁵ an expansion similar to the Σ^2 relation,⁴⁹ results in nonlinear functions. With the current developments in the area of operations research, however, such a function may be feasible in the near future.

As indicated by the speed of solution for the test case, it is quite possible to increase the size of the problem, adding more null point constraints and reducing truncation error by including more terms in the series. Such an increase, in itself, however, has not made a significant improvement in the tests run so far.

APPENDIX B: RESEARCH PROPOSALS

The following research proposals regard extensions of work reported in this thesis.

1. Although the coordination geometry of bis(2,2'-bipyridylamine) copper(II) perchlorate has been well established, a careful redetermination of the structure, with errors comparable to those in the structure of 2,2'-bipyridylamine, would provide data for a comparison between the coordinated and free ligand. The structure determination of bis(2,2'-bipyridylaminato) copper(II),⁵⁰ in which the amine protons have been removed leaving the ligand with a net negative charge, would allow the comparison to be carried further. Structural differences between the two similar metal complexes would also be of interest.

2. The structure determination of the high melting polymorph of 2,2'-bipyridylamine would provide information on the effect of structure on the macroscopic properties of this compound.

3. Further work on the method of phase determination mentioned in Appendix A is warranted with particular emphasis on the formulation of a more effective objective function.