Crystal and Molecular Structure of Amminebis-(2,2′-bipyridyl)copper(II) Tetrafluoroborate

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods from three-dimensional counter data. The structure was solved by Patterson and Fourier methods and refined by least-squares to R 0·087 for 2894 independent reflections. The complex crystallises in the monoclinic unit cell, space-group $P2_1/c$, with dimensions $a = 9{\cdot}051$, $b = 13{\cdot}493$, $c = 19{\cdot}278$ Å, $\beta = 103°\ 20'$, and $Z = 4$. The cation has C_2 symmetry and the environment about the copper atom is approximately trigonal bipyramidal. The trigonal plane is formed by a nitrogen atom from each bipyridyl ligand (Cu–N 2·09 Å, subtending an angle of 108° at Cu) and the ammonia molecule (Cu–NH_3 2·05 Å). The remaining bipyridyl nitrogen atoms occupy the axial positions (Cu–N 1·97 Å) and the direction between these two nitrogen atoms lies 11·4° from the normal to the trigonal plane.

THE electronic, e.s.r., and i.r. spectra of $[Cu(bipy)_2(NH_3)](BF_4)_2$ (bipy = 2,2′-bipyridyl) indicate the copper atom to be in an approximately trigonal bipyramidal environment.[1] Preliminary studies of the polarised single-crystal electronic spectra of this complex suggested that the molecular axes of the cations were aligned parallel in the unit cell.[2] The structure of the complex was undertaken to determine the precise environment about the copper atom and thereby yield detailed knowledge of the molecular geometry required for the interpretation of the electronic properties.

EXPERIMENTAL

Crystal Data.—$C_{20}H_{19}B_2CuF_8N_5$, $M = 566{\cdot}6$, Monoclinic, $a = 9{\cdot}051 \pm 0{\cdot}012$, $b = 13{\cdot}493 \pm 0{\cdot}022$, $c = 19{\cdot}278 \pm 0{\cdot}026$ Å, $\beta = 103°\ 20' \pm 5'$, $U = 2291{\cdot}0$ Å^3, $D_m = 1{\cdot}63$ (by flotation), $Z = 4$, $D_c = 1{\cdot}642$, $F(000) = 1140$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 10·8 cm^{-1}, for cell dimensions and intensity measurements. Space-group $P2_1/c$ (C^5_{2h}, No. 14).

The complex crystallises as blue diamond-shaped plates lying on (100) with pinacoids {011} and {01$\bar{1}$}. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. The intensities were measured at 22—26 °C on a Philips PAILRED diffractometer using monochromatised Mo-K_α radiation. Each reflection in the h0—18l layers, to a maximum angle of $\theta = 30°$, was recorded. 2894 Reflections gave counts for which $\sigma(I)/I < 0{\cdot}5$.[3] The intensities were corrected for Lorentz and polarisation effects, but no correction for absorption or extinction was applied.

Wilson's method[4] was used to place the data on an approximately absolute scale. The scattering-factor curves for all atoms were taken from ref. 5, the values for the copper atom being corrected for anomalous dispersion. All calculations were carried out on the computer at S.R.C. Chilton, with programmes of Hodgson, Mills, and Stephens.

Structure Determination.—The position of the copper atom was obtained from a three-dimensional Patterson synthesis. The complete solution of the structure was obtained by means of a series of Fourier syntheses, each phased on an increasing number of atoms. The structure factors calculated with co-ordinates for all non-hydrogen atoms and an overall thermal parameter $B = 3{\cdot}0$ Å^2 gave R 0·27. Refinement of the structure was carried out by use of a least-squares procedure in which the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The weight for each reflection, w, was unity for the initial refinement and was calculated from the expression $w = (20{\cdot}0 + 0{\cdot}2|F_o| + 0{\cdot}02|F_o|^2)^{-1}$ for the final refinement. For this latter weighting scheme the average values of Δ^2 for ranges of increasing $|F_o|$ were almost constant. Reflections, whose calculated structure factors were less than one-third of the observed values, were omitted from the least-squares analysis.

The initial refinement used a full-matrix technique in which positional and individual isotropic thermal parameters for each atom together with an overall scale factor were refined. A difference Fourier synthesis was calculated when the maximum shift in any parameter was of the order of its estimated standard deviation. This map indicated the approximate positions for 16 of the 19 hydrogen atoms. The positions of the hydrogen atoms of the ammonia could not be obtained. The positions of the 16 hydrogen atoms found were optimised, assuming C–H 1·00 Å, and in subsequent refinement were included with an isotropic thermal parameter of $B = 5{\cdot}75$ Å^2, but not refined. The difference map further indicated that the tetrafluoroborate ion B(2) had considerable anisotropic thermal motion particularly F(5) and F(8).

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. However, owing to the large number (326) of parameters being refined it was necessary to refine the parameters in six block matrices; matrices (1)—(6) contained the parameters for the overall scale and thermal parameter, the copper atom and ammonia nitrogen atom, each bipyridyl ring and each tetrafluoroborate ion. The refinement was terminated when the maximum shift in any parameter was $<0{\cdot}15\sigma$. 2868 Reflections were included in the final cycle of refinement. The final values of R, based on 2894 reflections, and R' [$= \Sigma w\Delta^2/\Sigma w|F_o|^2$] were 0·087 and 0·014 respectively.

The final atomic co-ordinates and thermal parameters together with their estimated standard deviations are given in Tables 1 and 2 respectively. Observed and calculated structure factors are listed in Supplementary Publication No. SUP. 20391 (17 pp., 1 microfiche)†.

DISCUSSION

Table 3 gives the bond distances and angles together with their estimated standard deviations derived

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[1] R. C. Slade, A. A. G. Tomlinson, B. J. Hathaway, and D. E. Billing, *J. Chem. Soc.* (*A*), 1968, 61.

[2] B. J. Hathaway, personal communication.

[3] M. Mack, *Norelco Reporter*, 1965, **12**, 40.

[4] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[5] 'International Tables for *X*-Ray Crystallography, vol. III, Kynoch Press, Birmingham, 1962.

directly from the least-squares inverse matrices. The structure consists of discrete $[Cu(bipy)_2(NH_3)]^{2+}$ and BF_4^- ions the packing of which in the crystal together with the labelling of the atoms is shown in the Figure. The two independent BF_4^- ions are hydrogen bonded to the ammonia group of the $[Cu(bipy)_2(NH_3)]^{2+}$ ion as shown in the Figure; the B(1) ion forms four such bonds and the B(2) only two. A further five contacts may be considered as weak hydrogen bonds of the type F · · · HC and these are listed in Table 4. Considering the overall hydrogen-bonding network, three of the fluorine atoms of the B(1) ion are involved, whereas for the B(2) ion only F(6) and F(7) are involved. The arrangement about the B(2) ion would allow it a freedom of motion such as an oscillation about an axis defined by F(6) and

TABLE 1

Atomic co-ordinates (fractional) with estimated standard deviations in parentheses

	x/a	y/b	z/c	σ_{rms}(Å)
Cu	0·0546(1)	0·2362(1)	0·1394(1)	0·0010
N(5)	0·0594(10)	0·0846(5)	0·1394(5)	0·008
N(1)	−0·0846(8)	0·2377(5)	0·2051(4)	0·007
C(1)	−0·2209(12)	0·1894(9)	0·1917(6)	0·011
C(2)	−0·3108(11)	0·1892(9)	0·2388(6)	0·011
C(3)	−0·2645(12)	0·2404(8)	0·3021(5)	0·010
C(4)	−0·1269(12)	0·2897(8)	0·3164(5)	0·010
C(5)	−0·0394(10)	0·2855(6)	0·2677(4)	0·008
C(6)	−0·1118(10)	0·3310(6)	0·2786(4)	0·008
C(7)	0·1813(12)	0·3804(7)	0·3422(4)	0·009
C(8)	0·3287(12)	0·4163(7)	0·3475(5)	0·010
C(9)	0·3978(12)	0·4076(7)	0·2933(6)	0·010
C(10)	0·3191(12)	0·3606(7)	0·2304(5)	0·010
N(2)	0·1834(8)	0·3210(5)	0·2241(4)	0·007
N(3)	0·1921(8)	0·2454(5)	0·0747(4)	0·007
C(11)	0·3285(11)	0·3008(8)	0·0851(5)	0·010
C(12)	0·4219(12)	0·2086(8)	0·0389(6)	0·011
C(13)	0·3767(11)	0·2661(7)	−0·0195(5)	0·010
C(14)	0·2370(12)	0·3122(7)	−0·0328(5)	0·010
C(15)	0·1462(10)	0·2008(6)	0·0150(4)	0·008
C(16)	−0·0027(11)	0·3463(6)	0·0075(5)	0·009
C(17)	−0·0761(12)	0·3992(6)	−0·0525(5)	0·010
C(18)	−0·2163(14)	0·4388(7)	−0·0541(6)	0·011
C(19)	−0·2798(13)	0·4258(7)	0·0034(7)	0·012
C(20)	−0·2044(11)	0·3735(7)	0·0606(6)	0·010
N(4)	−0·0656(8)	0·3326(5)	0·0634(4)	0·007
B(1)	−0·2365(12)	0·0938(8)	−0·0276(5)	0·011
F(1)	−0·2479(9)	0·0685(7)	0·0395(3)	0·008
F(2)	−0·2961(9)	0·0262(6)	−0·0778(4)	0·008
F(3)	−0·3110(9)	0·1810(5)	−0·0466(4)	0·008
F(4)	−0·0855(7)	0·1059(5)	−0·0277(3)	0·007
B(2)	0·3307(18)	0·0500(11)	0·3057(7)	0·015
F(5)	0·4176(15)	0·0982(20)	0·3553(8)	0·020
F(6)	0·3591(9)	0·0713(8)	0·2492(4)	0·009
F(7)	0·1830(9)	0·0610(9)	0·3100(5)	0·010
F(8)	0·3869(23)	−0·0387(13)	0·3239(12)	0·020
H(1)	−0·256	0·149	0·147	
H(2)	−0·407	0·146	0·227	
H(3)	−0·335	0·249	0·336	
H(4)	−0·090	0·331	0·361	
H(7)	0·135	0·382	0·384	
H(8)	0·373	0·454	0·394	
H(9)	0·504	0·437	0·296	
H(10)	0·363	0·348	0·189	
H(11)	0·371	0·158	0·130	
H(12)	0·525	0·174	0·049	
H(13)	0·441	0·281	−0·055	
H(14)	0·205	0·351	−0·078	
H(17)	−0·030	0·413	−0·095	
H(18)	−0·263	0·477	−0·097	
H(19)	−0·387	0·457	0·002	
H(20)	−0·247	0·361	0·103	

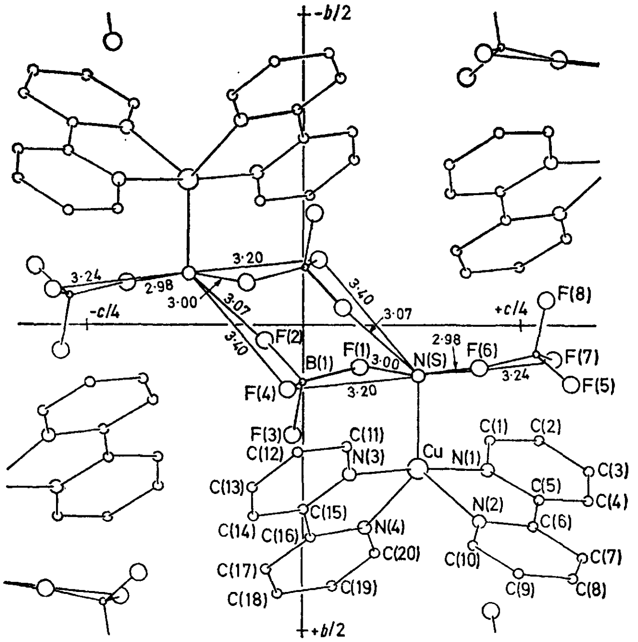
TABLE 2

Thermal parameters (× 10⁴) * with estimated standard deviations in parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	91·6(11)	43·0(5)	18·8(2)	0·7(8)	18·1(4)	−4·8(4)
N(5)	135(12)	35(4)	37(3)	−2(6)	26(5)	−1(3)
N(1)	116(10)	49(4)	21(2)	−11(6)	18(4)	−13(3)
C(1)	127(15)	77(7)	31(3)	−22(9)	25(6)	−13(4)
C(2)	105(14)	78(7)	32(3)	−6(8)	17(6)	2(4)
C(3)	135(14)	60(6)	33(3)	13(8)	34(5)	8(4)
C(4)	142(15)	67(7)	24(3)	15(8)	27(5)	−6(3)
C(5)	106(12)	33(4)	22(2)	12(6)	17(4)	2(2)
C(6)	97(11)	31(3)	19(2)	19(6)	7(4)	3(3)
C(7)	159(16)	41(5)	18(2)	10(7)	9(5)	−5(3)
C(8)	156(17)	43(5)	23(3)	1(8)	−9(5)	−8(3)
C(9)	113(14)	45(5)	39(4)	−18(7)	−1(6)	−6(4)
C(10)	136(15)	54(6)	25(3)	14(8)	9(5)	−3(3)
N(2)	114(11)	40(4)	20(2)	3(5)	19(4)	−3(2)
N(3)	97(9)	47(5)	24(3)	7(5)	17(4)	0(2)
C(11)	98(13)	69(6)	28(3)	20(8)	17(5)	−4(4)
C(12)	125(15)	64(7)	37(4)	3(8)	33(6)	−6(4)
C(13)	141(14)	51(5)	31(3)	−18(8)	37(5)	−4(3)
C(14)	159(16)	42(5)	26(3)	−6(7)	31(5)	0(3)
C(15)	124(13)	30(4)	19(2)	−1(6)	7(4)	−4(2)
C(16)	115(12)	27(4)	24(2)	−4(6)	7(4)	−8(3)
C(17)	150(16)	34(4)	25(3)	2(7)	−1(5)	1(3)
C(18)	196(20)	34(5)	36(4)	−9(8)	−39(7)	3(4)
C(19)	136(16)	35(5)	56(5)	21(8)	10(7)	−3(4)
C(20)	115(14)	36(5)	39(4)	15(7)	9(6)	−8(3)
N(4)	85(9)	33(3)	26(2)	1(5)	11(4)	−7(2)
B(1)	104(14)	47(6)	25(3)	11(7)	18(5)	−4(3)
F(1)	214(13)	156(8)	28(2)	−8(8)	31(4)	21(3)
F(2)	226(13)	94(6)	52(3)	−15(7)	18(5)	−41(3)
F(3)	260(14)	64(4)	58(3)	50(7)	56(6)	17(3)
F(4)	123(9)	104(5)	38(2)	16(6)	22(4)	17(3)
B(2)	200(25)	80(9)	28(4)	5(12)	30(8)	−6(5)
F(5)	320(28)	574(39)	110(8)	−47(26)	4(12)	−195(15)
F(6)	180(13)	207(10)	46(3)	49(9)	36(5)	36(5)
F(7)	187(14)	208(11)	52(3)	2(10)	47(5)	12(5)
F(8)	802(53)	222(17)	222(14)	227(27)	334(25)	150(14)

For all hydrogen atoms $B = 5{\cdot}75$ Å²

* The anisotropic thermal parameters are given by: $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.



The packing of the ions in the crystal together with the labelling of the atoms. The thin lines indicate the hydrogen bonding between the ammonia and the BF_4^- ions

F(7). This type of motion is in accord with the high thermal parameters associated with F(5) and F(8) and could account for the shortened B–F distances for these atoms.

TABLE 3

Bond lengths and angles with estimated standard deviations in parentheses

(*a*) Distances (Å)

Cu(–N(2)	2·112(7)	Cu–N(1)	1·982(7)
Cu–N(4)	2·070(7)	Cu–N(3)	1·958(7)
Cu–N(5)	2·045(7)		
N(1)–C(1)	1·366(12)	N(3)–C(11)	1·346(11)
C(1)–C(2)	1·352(13)	C(11)–C(12)	1·366(13)
C(2)–C(3)	1·380(15)	C(12)–C(13)	1·349(15)
C(3)–C(4)	1·383(14)	C(13)–C(14)	1·379(14)
C(4)–C(5)	1·362(11)	C(14)–C(15)	1·378(12)
C(5)–N(1)	1·346(10)	C(15)–N(3)	1·355(11)
C(5)–C(6)	1·471(12)	C(15)–C(16)	1·457(12)
C(6)–C(7)	1·409(11)	C(16)–C(17)	1·391(12)
C(7)–C(8)	1·400(14)	C(17)–C(18)	1·370(16)
C(8)–C(9)	1·341(15)	C(18)–C(19)	1·372(17)
C(9)–C(10)	1·407(13)	C(19)–C(20)	1·355(15)
C(10)–N(2)	1·319(12)	C(20)–N(4)	1·361(11)
N(2)–C(6)	1·363(10)	N(4)–C(16)	1·344(11)
B(1)–F(1)	1·364(11)	B(2)–F(5)	1·269(18)
B(1)–F(2)	1·350(12)	B(2)–F(6)	1·325(14)
B(1)–F(3)	1·363(12)	B(2)–F(7)	1·367(16)
B(1)–F(4)	1·376(12)	B(2)–F(8)	1·317(18)

(*b*) Angles (°)

N(2)–Cu–N(4)	108·2(3)	N(1)–Cu–N(4)	97·9(3)
N(2)–Cu–N(5)	122·3(3)	N(1)–Cu–N(5)	91·6(3)
N(4)–Cu–N(5)	129·5(3)	N(1)–Cu–N(2)	79·6(3)
N(1)–Cu–N(3)	175·7(3)	N(3)–Cu–N(4)	79·5(3)
N(3)–Cu–N(5)	92·7(3)	N(2)–Cu–N(3)	98·0(3)
Cu–N(1)–C(1)	123·6(6)	Cu–N(3)–C(11)	125·0(6)
Cu–N(1)–C(5)	118·2(6)	Cu–N(3)–C(15)	117·4(6)
C(5)–N(1)–C(1)	118·1(7)	C(15)–N(3)–C(11)	117·6(7)
N(1)–C(1)–C(2)	122·1(9)	N(3)–C(11)–C(12)	123·6(9)
C(1)–C(2)–C(3)	119·0(10)	C(11)–C(12)–C(13)	118·3(9)
C(2)–C(3)–C(4)	119·6(8)	C(12)–C(13)–C(14)	120·3(8)
C(3)–C(4)–C(5)	118·8(9)	C(13)–C(14)–C(15)	119·1(8)
C(4)–C(5)–N(1)	122·3(8)	C(14)–C(15)–N(3)	121·1(8)
C(6)–C(5)–N(1)	114·1(7)	C(16)–C(15)–N(3)	114·4(7)
C(4)–C(5)–C(6)	123·6(7)	C(14)–C(15)–C(16)	124·5(8)
C(5)–C(6)–C(7)	122·4(8)	C(15)–C(16)–C(17)	123·6(8)
C(5)–C(6)–N(2)	116·1(7)	C(15)–C(16)–C(4)	114·6(7)
N(2)–C(6)–C(7)	121·4(8)	N(4)–C(16)–C(17)	121·9(9)
C(6)–C(7)–C(8)	117·0(8)	C(16)–C(17)–C(18)	118·8(9)
C(7)–C(8)–C(9)	121·3(8)	C(17)–C(18)–C(19)	119·4(9)
C(8)–C(9)–C(10)	118·5(9)	C(18)–C(19)–C(20)	119·8(10)
C(9)–C(10)–N(2)	122·5(9)	C(19)–C(20)–N(4)	122·0(10)
C(10)–N(2)–C(6)	119·1(7)	C(20)–N(4)–C(16)	118·1(8)
Cu–N(2)–C(6)	112·0(5)	Cu–N(4)–C(16)	113·8(6)
Cu–N(2)–C(10)	128·9(6)	Cu–N(4)–C(20)	127·8(6)
F(1)–B(1)–F(2)	113·9(9)	F(5)–B(2)–F(6)	111·1(16)
F(1)–B(1)–F(3)	109·3(8)	F(5)–B(2)–F(7)	110·1(12)
F(1)–B(1)–F(4)	108·9(9)	F(5)–B(2)–F(8)	97·6(18)
F(2)–B(1)–F(3)	107·4(9)	F(6)–B(2)–F(7)	115·5(12)
F(2)–B(1)–F(4)	108·1(8)	F(6)–B(2)–F(8)	107·3(13)
F(3)–B(1)–F(4)	109·1(8)	F(7)–B(2)–F(8)	113·9(14)

The [Cu(bipy)$_2$(NH$_3$)]$^{2+}$ ion has approximately C_2 symmetry, the direction of the C_2 axis being colinear with the Cu–N(5) direction. Each bipyridyl ligand acts as a bidentate chelate through the nitrogen atoms, and the ammonia molecule completes five-co-ordination about the copper atom. The environment of the copper atom is approximately trigonal bipyramidal, the N(1)–N(3) axial direction lying 11·4° from the normal to the trigonal plane. The two Cu–N distances for a given bipyridyl ligand are significantly different but the corresponding bonds from the two ligands are equivalent. The mean values for these two Cu–N bonds are 1·97 and 2·09 Å, respectively. The two shorter Cu–N bonds are almost colinear and the remaining two subtend an angle of 108° at the copper atom. The internal bipyridyl nitrogens subtend an angle of 79·5°. This arrangement of the bipyridyl ligands about the copper atom closely resembles the corresponding arrangements found in [Cu(bipy)$_2$I]I [6] and [Cu(bipy)$_2$(ONO)]NO$_3$.[7]

TABLE 4

F · · · HC contacts

	F · · · C	F · · · H *	Angle F · · · H–C
C(1) · · · F(1)	3·32 Å	2·35 Å	159°
C(2) · · · F(6^{I})	3·40	2·43	157
C(4) · · · F(4^{II})	3·26	2·29	166
C(11) · · · F(6)	3·46	2·50	155
C(14) · · · F(7^{III})	3·41	2·44	168

* Hydrogen-atom positions calculated assuming C–H 1·00 Å. Roman numerals as superscripts refer to the following equivalent positions relative to the atoms at x, y, z:

I $x - 1, y, z$

II $x, \frac{1}{2} - y, \frac{1}{2} + z$

III $x, \frac{1}{2} - y, z - \frac{1}{2}$

TABLE 5

Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X', Y', and Z' are orthogonal co-ordinates related to the atomic co-ordinates X, Y, and Z by $X' = X \sin \beta$, $Y' = Y$ and $Z' = Z + X \cos \beta$. The deviations (Å) of the most relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
Plane (1):				
Cu, N(2), N(4), N(5)	−0·7619	−0·0179	0·6474	1·2410
[Cu 0·0015, N(2), −0·0004, N(4) −0·0005, N(5) −0·0005]				
Plane (2):				
N(1), C(1)—(5)	−0·4528	0·8265	−0·3346	1·5995
[N(1) 0·007, C(1) 0·003, C(2) −0·008, C(3) 0·003, C(4) 0·007, C(5) −0·013]				
Plane (3):				
N(2), C(6)—(10)	−0·3950	0·8706	−0·2932	1·9967
[N(2) −0·017, C(6) −0·003, C(7) 0·018, C(8) −0·013, C(9) −0·007, C(10) 0·0023]				
Plane (4):				
N(3), C(11)—(15)	0·4286	0·8020	0·4160	3·8065
[N(3) 0·006, C(11) 0·003, C(12) −0·011, C(13) 0·011, C(14) −0·002, C(15) −0·007]				
Plane (5):				
N(4), C(16)—(20)	0·4357	0·8410	0·3208	3·9636
[N(4) −0·005, C(16) 0·004, C(17) 0·001, C(18) −0·004, C(19) 0·003, C(20) 0·002]				

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[6] G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691.

[7] F. S. Stephens and I. M. Procter, *J. Chem. Soc.* (*A*), 1968, 1248.

The bond lengths and angles within the bipyridyl ligands are in accordance with those previously reported.[6-8] The bipyridyl ligands are not planar but each individual pyridyl ring is planar (see Table 5). The pyridyl rings of a given bipyridyl ligand are twisted about the 2,2'-bond by 4·8 and 5·9° for the ligands defined by N(1), N(2) and by N(3), N(4), respectively. These values are significantly smaller than those of 11—12° in $[Cu(bipy)_2(ONO)]NO_3$ [7] and of 10° in $[Cu(bipy)_2I]I$.[6]

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[8] *Chem. Soc. Special Publ.*, No. 11, 1959, and No. 18, 1965.