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The Crystal Structure of Bis(2,2′-bipyridine)-*catena*-μ-tetrafluoroborato-copper(II) Tetrafluoroborate

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The crystal structure of the title compound was determined by means of the X-ray diffraction technique. The crystal is triclinic, space group P$\bar{1}$, a=11.288(8), b=15.186(17), c=7.368(4) Å, α=74.93(3), β=78.23(3), γ=65.92(3)°, and Z=2. The structure was solved by the heavy-atom method and refined by the least-squares method to R=0.068 for 3678 non-zero reflections. The crystal is composed of BF_4^- ions and polymeric chains of $[Cu(BF_4)(bpy)_2{}^+]$ in which a tetrafluoroborate ion bridges two adjacent copper atoms through its two fluorine atoms. The coordination polyhedron around the copper atom is a tetragonally distorted octahedron; the four nitrogen atoms of bipyridine molecules in the equatorial plane are arranged in a flattened tetrahedral manner (average Cu–N=1.99 Å) and the two axial Cu–F distances are 2.566(6) and 2.662(4) Å. In both bipyridine molecules, the two pyridine rings are twisted slightly from each other; the interplanar angle is 3.1° in one bipyridine ligand and 10.2° in the other.

Since the crystal structure of [CuI(bpy)$_2$]I was reported in 1963,[1)] bis(bipyridine)copper(II) complexes have attracted much attention because of the diversity of their stereochemistry. They have been shown to take various stereochemistries such as distorted trigonal bipyramid,[1–3)] distorted square pyramid,[4–6)] and *cis*- and *trans*-distorted octahedra.[7–10,22)] Recently, some attempts to understand such changes in coordination geometry have been made.[4–5)]

In this paper, as a part of our structural study on bis(bipyridine)copper(II) complexes, the crystal structure of $[Cu(BF_4)(bpy)_2]BF_4$ will be reported and the structures of some bis(bipyridine)copper(II) complexes will be discussed in terms of the sense of distortion illustrated in Fig. 3.

Experimental

Blue crystals of $[Cu(BF_4)(bpy)_2]BF_4$ were prepared by adding a methanol solution of 2,2′-bipyridine (20 mmol in 30 cm^3 of the solvent) to an aqueous solution of copper(II) tetrafluoroborate (10 mmol in 30 cm^3 of water), and were recrystallized from a water–methanol mixture. Found: C, 43.53; H, 2.99; N, 10.19%. Calcd for $Cu(bpy)_2(BF_4)_2$: C, 43.72; H, 2.93; N, 10.20%.

Preliminary X-ray photographs taken with Cu *Kα* radiation showed $\bar{1}$ Laue symmetry, indicating a triclinic space group. No systematic absences were observed. The space group P$\bar{1}$ was confirmed by a successful refinement of the structure.

A crystal was shaped into a sphere 0.30 mm in diameter and used for data collection. The lattice constants were determined by a least-squares fit using 45 independent θ-values measured accurately on a diffractometer. Crystal data: $[Cu(BF_4)(bpy)_2]BF_4$, *M.W.*=549.5, triclinic, space group P$\bar{1}$, a=11.288(8), b=15.186(17), c=7.368(4) Å, α=74.93(3), β=78.23(3), γ=65.92(3)°, U=1106.5 Å^3, Z=2, D_c=1.65, D_m=1.65 g cm^{-3} (by flotation in a benzene–bromoform mixture), Mo *Kα* radiation (λ=0.71069 Å), μ(Mo *Kα*)=10.7 cm^{-1}.

Intensity data with $2\theta \leqq 55°$ were collected at room temperature by means of the ω-2θ scan techniques on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo *Kα* radiation. The scan speed and scan width were 0.033° s^{-1} and $(1.00+0.20 \tan\theta)°$ respectively. Background counts were measured for scantime/2 at each side of the scan range. A total of 5125 reflections having $I_t - 2\sqrt{I_t} > I_b$ were collected; I_t is the intensity (counts/s) measured at the top of the peak, while I_b is the mean background measurement for 5 s at each side of the peak, but 3678 reflections for which $F_o{}^2 > 2\sigma(F_o{}^2)$ were used in the structure analysis. Intensity data were corrected for the *Lp* factor[11)] but not for absorption.

Structure Determination

The structure was solved by the heavy-atom method. The positions of the copper atoms were determined from a three-dimensional Patterson map; all the other non-hydrogen atoms were successively located by means of Fourier syntheses. The positional and thermal parameters were refined by the use of the block-diagonal least-squares method. The minimized function was $\sum w(F_o - |F_c|)^2$. A weighting scheme of the type suggested by Hughes[12)] was applied using w=1.0 for $F_o \leqq 120.0$ and $w=(120.0/F_o)^2$ for $F_o > 120.0$. The atomic scattering factors were taken from Ref. 13. The positions of hydrogen atoms were obtained from a difference Fourier synthesis. These hydrogen atoms were included in the final refinement with isotropic thermal parameter of 4.0 Å^2. In the final cycle of the refinement, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value was 0.068 for 3678 non-zero reflections. The final atomic parameters are summarized in Tables 1 and 2 with averaged isotropic temperature factors. The anisotropic thermal parameters for non-hydrogen atoms and complete lists of the F_o and $|F_c|$ values have been preserved by the Chemical Society of Japan (Document No. 8320). All computations were carried out on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The computer programs used in the calculation were as follows: HBLS-V[14)] (least-squares calculation), RSSFR-5[15)] (Fourier synthesis), and DAPH[14)] (interatomic distances and coordinates of the H atoms).

Results and Discussion

The crystal structure of $[Cu(BF_4)(bpy)_2]BF_4$ consists of tetrafluoroborate ions and polymeric chains of $[Cu(BF_4)(bpy)_2{}^+]$ approximately parallel to the c axis, in which Cu(bpy)$_2$-moieties are bridged by tetrafluoro-

TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} a)	Atom	*x*	*y*	*z*	B_{eq}/Å^{2} a)
Cu	1398.1 (7)	2389.1 (5)	4001.3 (10)	3.75	C(15)	1905 (5)	371 (4)	5316 (7)	3.83
N(1)	1920 (5)	3536 (4)	3579 (7)	4.42	C(16)	3096 (5)	422 (4)	4079 (7)	3.75
C(1)	3051 (7)	3514 (5)	3914 (10)	6.32	C(17)	4133 (6)	−399 (5)	3607 (9)	4.93
C(2)	3304 (9)	4379 (7)	3548 (11)	8.27	C(18)	5197 (6)	−274 (5)	2422 (9)	5.61
C(3)	2368 (10)	5250 (6)	2870 (10)	8.60	C(19)	5187 (6)	654 (5)	1734 (8)	5.51
C(4)	1192 (9)	5282 (5)	2599 (9)	6.87	C(20)	4111 (6)	1452 (5)	2229 (8)	4.53
C(5)	979 (7)	4403 (4)	2986 (8)	5.00	N(4)	3099 (4)	1333 (3)	3412 (6)	3.23
C(6)	−250 (6)	4356 (4)	2793 (7)	4.45	B(1)	1279 (7)	2090 (5)	9241 (9)	4.19
C(7)	−1314 (7)	5163 (5)	2104 (9)	5.95	F(1)	1738 (5)	2318 (3)	7383 (5)	8.07
C(8)	−2423 (7)	5042 (6)	1958 (10)	6.87	F(2)	1582 (4)	2611 (3)	10262 (5)	6.03
C(9)	−2488 (6)	4119 (6)	2497 (10)	6.34	F(3)	1822 (4)	1106 (3)	9914 (6)	6.84
C(10)	−1390 (6)	3338 (5)	3170 (9)	5.33	F(4)	−60 (4)	2378 (3)	9409 (7)	7.27
N(2)	−308 (5)	3453 (3)	3348 (6)	3.76	B(11)	5881 (11)	2798 (8)	7457 (23)	10.63
N(3)	915 (4)	1249 (3)	5353 (6)	3.36	F(11)	4801 (5)	2622 (4)	7932 (10)	11.90
C(11)	−187 (6)	1278 (4)	6469 (8)	4.59	F(22)	5612 (7)	3758 (5)	7004 (14)	17.16
C(12)	−351 (7)	431 (5)	7561 (9)	5.64	F(33)	6264 (10)	2557 (6)	5542 (14)	19.95
C(13)	651 (7)	−464 (5)	7529 (9)	5.81	F(44)	6799 (7)	2223 (8)	8354 (18)	23.19
C(14)	1802 (7)	−496 (4)	6390 (9)	5.13					

a) Equivalent isotropic temperature factor (W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959)).

TABLE 2. ATOMIC COORDINATES ($\times 10^3$) FOR HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H(C1)	371(6)	283(5)	423(9)	H(C11)	−87(6)	196(5)	664(9)
H(C2)	409(6)	422(5)	386(9)	H(C12)	−117(6)	42(5)	812(9)
H(C3)	251(6)	584(5)	266(9)	H(C13)	52(6)	−110(5)	826(9)
H(C4)	46(6)	593(5)	224(9)	H(C14)	241(6)	−111(5)	624(9)
H(C7)	−112(6)	576(5)	177(9)	H(C17)	406(6)	−101(5)	400(9)
H(C8)	−319(6)	561(5)	139(9)	H(C18)	597(6)	−82(5)	218(9)
H(C9)	−323(6)	390(5)	228(9)	H(C19)	581(6)	80(5)	93(9)
H(C10)	−140(6)	263(5)	335(9)	H(C20)	409(6)	210(5)	182(9)

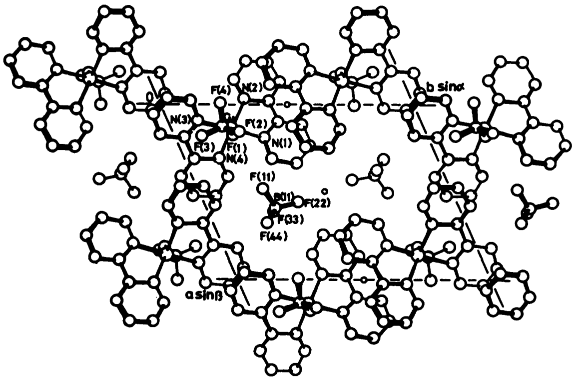


Fig. 1. Crystal structure viewed down the c axis.

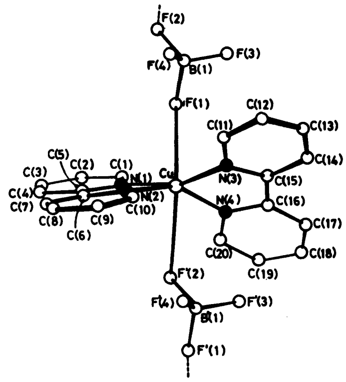


Fig. 2. A schematic drawing of a part of the infinite chain, $[Cu(BF_4)(bpy)_2{}^+]_\infty$.

borate ligands through the F atoms, as shown in Figs. 1 and 2. The bond lengths and angles with their estimated standard deviations are given in Table 3.

In the complex cation, the coordination polyhedron around the copper atom is a distorted *trans*-octahedron, in which four N atoms of the two bpy chelates form an equatorial plane (mean Cu–N = 1.99 Å) and two F atoms of bridging BF_4^- ions occupy the axial positions (Cu–F(1) = 2.566(6) Å and Cu–F(2) = 2.662(4) Å). Although the four N atoms are arranged around the copper atom in a flattened tetrahedral manner, the copper atom lies almost on the least-squares plane defined by these nitrogen atoms (Table 5). Such a tetrahedral distortion of planar $Cu(bpy)_2$-moiety is now well-known to be due to the steric repulsions between the hydrogen atoms on 6- and 6′-carbon atoms of the bpy chelates. The dihedral angle between the (N(1)–Cu–N(2)) and (N(3)–Cu–N(4)) planes is 36.1°. Analogous stereochemistries have been found in $[Cu(ClO_4)(bpy)_2]ClO_4$[8]

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Interatomic distance	l/Å		l/Å
Cu-N(1)	1.989(6)	C(16)-C(17)	1.384(9)
Cu-N(2)	1.996(5)	C(17)-C(18)	1.384(10)
Cu-N(3)	1.985(5)	C(18)-C(19)	1.363(11)
Cu-N(4)	1.989(5)	C(19)-C(20)	1.388(11)
Cu-F(1)	2.566(6)	B(1)-F(1)	1.369(9)
Cu-F′(2)	2.662(4)	B(1)-F(2)	1.394(9)
N(1)-C(1)	1.335(10)	B(1)-F(3)	1.359(9)
N(1)-C(5)	1.342(9)	B(1)-F(4)	1.379(9)
C(1)-C(2)	1.404(13)	B(11)-F(11)	1.31(2)
C(2)-C(3)	1.360(15)	B(11)-F(22)	1.33(2)
C(3)-C(4)	1.362(15)	B(11)-F(33)	1.49(2)
C(4)-C(5)	1.398(12)	B(11)-F(44)	1.23(2)
C(5)-C(6)	1.455(10)	C(1)-H(C1)	1.00(7)
N(2)-C(6)	1.350(9)	C(2)-H(C2)	0.88(7)
N(2)-C(10)	1.338(9)	C(3)-H(C3)	0.94(7)
C(6)-C(7)	1.388(11)	C(4)-H(C4)	1.00(7)
C(7)-C(8)	1.366(12)	C(7)-H(C7)	0.98(7)
C(8)-C(9)	1.382(13)	C(8)-H(C8)	1.01(7)
C(9)-C(10)	1.391(12)	C(9)-H(C9)	1.08(7)
N(3)-C(11)	1.335(8)	C(10)-H(C10)	1.06(7)
N(3)-C(15)	1.348(8)	C(11)-H(C11)	1.03(7)
C(11)-C(12)	1.389(10)	C(12)-H(C12)	0.94(7)
C(12)-C(13)	1.371(11)	C(13)-H(C13)	1.03(7)
C(13)-C(14)	1.386(11)	C(14)-H(C14)	0.92(7)
C(14)-C(15)	1.385(10)	C(17)-H(C17)	0.93(7)
C(15)-C(16)	1.481(8)	C(18)-H(C18)	0.96(7)
N(4)-C(16)	1.342(8)	C(19)-H(C19)	0.89(7)
N(4)-C(20)	1.333(8)	C(20)-H(C20)	0.94(7)

Bond angle	ϕ/°		ϕ/°
F(1)-Cu-N(1)	79.6(2)	F(1)-Cu-N(2)	109.8(2)
F(1)-Cu-N(3)	80.3(2)	F(1)-Cu-N(4)	96.7(2)
F′(2)-Cu-N(1)	88.1(2)	F′(2)-Cu-N(2)	76.9(2)
F′(2)-Cu-N(3)	112.1(2)	F′(2)-Cu-N(4)	76.9(2)
N(1)-Cu-N(2)	81.8(2)	N(1)-Cu-N(3)	159.8(2)
N(1)-Cu-N(4)	101.5(2)	N(2)-Cu-N(3)	103.5(2)
N(2)-Cu-N(4)	153.5(2)	N(3)-Cu-N(4)	82.5(2)
C(1)-N(1)-C(5)	119.6(6)	N(1)-C(1)-C(2)	121.0(8)
C(1)-C(2)-C(3)	119.0(9)	C(2)-C(3)-C(4)	120.2(10)
C(3)-C(4)-C(5)	118.9(9)	N(1)-C(5)-C(4)	121.1(7)
N(1)-C(5)-C(6)	115.5(6)	C(4)-C(5)-C(6)	123.4(7)
Cu-N(1)-C(1)	126.5(5)	Cu-N(1)-C(5)	113.8(5)
Cu-N(2)-C(6)	113.2(4)	Cu-N(2)-C(10)	126.9(5)
C(6)-N(2)-C(10)	119.2(6)	C(5)-C(6)-N(2)	115.3(6)
C(5)-C(6)-C(7)	124.2(7)	N(2)-C(6)-C(7)	120.6(6)
C(6)-C(7)-C(8)	119.8(8)	C(7)-C(8)-C(9)	120.1(8)
C(8)-C(9)-C(10)	117.4(8)	N(2)-C(10)-C(9)	122.8(7)
C(11)-N(3)-C(15)	118.7(5)	N(3)-C(11)-C(12)	122.0(6)
C(11)-C(12)-C(13)	119.6(7)	C(12)-C(13)-C(14)	118.6(7)
C(13)-C(14)-C(15)	119.3(7)	N(3)-C(15)-C(14)	121.8(6)
N(3)-C(15)-C(16)	114.5(5)	C(14)-C(15)-C(16)	123.7(6)
Cu-N(3)-C(11)	126.8(4)	Cu-N(3)-C(15)	113.7(4)
Cu-N(4)-C(16)	113.4(4)	Cu-N(4)-C(20)	126.4(4)
C(16)-N(4)-C(20)	119.3(5)	C(15)-C(16)-N(4)	115.1(5)
C(15)-C(16)-C(17)	123.2(6)	N(4)-C(16)-C(17)	121.7(6)
C(16)-C(17)-C(18)	118.8(6)	C(17)-C(18)-C(19)	119.2(7)
C(18)-C(19)-C(20)	119.4(7)	N(4)-C(20)-C(19)	121.5(7)
F(1)-B(1)-F(2)	108.1(6)	F(1)-B(1)-F(3)	110.5(6)
F(1)-B(1)-F(4)	109.6(6)	F(2)-B(1)-F(3)	110.8(6)
F(2)-B(1)-F(4)	108.7(6)	F(3)-B(1)-F(4)	109.2(6)
F(11)-B(11)-F(22)	111(2)	F(11)-B(11)-F(33)	100(2)
F(11)-B(11)-F(44)	115(2)	F(22)-B(11)-F(33)	100(2)
F(22)-B(11)-F(44)	122(2)	F(33)-B(11)-F(44)	104(2)

F′(2) atom is related by the symmetry code $(x, y, -1+z)$ to F(2) atom.

TABLE 4. SOME BOND LENGTHS AND ANGLES OF $[CuN_4X_2]$- AND $[CuN_4X]$-CHROMOPHORES (X=N, O, OR F) IN BIS(BIPYRIDINE)COPPER(II) COMPLEXES[a)] (See Fig. 3 for notation)

	Complex	Bond length l/Å			Bond angle ϕ/°				Ref.
		Cu-N(bpy)	Cu-X(1)	Cu-X(2)	θ_1	θ_2	ϕ_1	ϕ_2	
1	$[Cu(S_3O_6)(bpy)_2]$	1.98 —1.99	2.82	2.82					9
2	$[Cu(S_4O_6)(bpy)_2]$	1.985—1.995	2.627	2.627	155.2[b)]	155.2[b)]			10
3	$[Cu(BF_4)(bpy)_2]BF_4$	1.985—1.996	2.566	2.662	159.8	153.5			This work
4	$[Cu(ClO_4)(bpy)_2]ClO_4$[c)]	1.97—2.02	2.45	2.73	161.1	151.0			8
5	$[Cu(NO_3)(bpy)_2]NO_3\cdot H_2O$	1.982—2.045	2.299		170.9	140.2			4
		1.973—2.051	2.301		170.7	140.7			4
6	$[Cu(S_2O_8)(bpy)_2]\cdot H_2O$	1.959—2.039	2.367		172.2	141.0			5
7	$[Cu(H_2O)(phen)_2](BF_4)_2$[d)]	1.985—2.041	2.238		172.8	136.6			16
8	$[Cu(H_2O)(bpy)_2]S_2O_6$[c)]	1.98—2.01	2.16		174.6	129.8			2
9	$[Cu(NH_3)(bpy)_2](BF_4)_2$	1.958—2.112	2.045		184.3	108.2	129.5	122.3	3
10	$[Cu(NCS)(bpy)_2]BF_4$	1.980—2.120	1.967		185.3	104.6	137.9	117.5	17
11	$[Cu_2(pydca)_2(bpy)_2]\cdot 4H_2O$[d)]	1.985—2.115	2.029		182.5[b)]	108.7	138.9	112.4	19
12	$[Cu(H_2O)(bpy)_2]S_5O_6$	1.973—2.123	2.054		180.9	111.4	143.6	104.9	6
13	$[Cu(HCOO)(bpy)_2]BF_4\cdot 0.5H_2O$	1.978—2.158	2.024		184.2	113.2	146.1	100.5	20
14	$[Cu(CH_3COO)(bpy)_2]ClO_4\cdot H_2O$	1.971—2.168	2.031		185.5	111.6	147.6	100.7	21
15	$[Cu(CH_3COO)(bpy)_2]BF_4$	1.995—2.209	1.980		181.7	111.0	156.5	92.3	21

a) Distorted *cis*-octahedral $[Cu(NO_2)(bpy)_2]Y$ complexes ($Y=NO_3$[7)] and BF_4[22)]) are not included. b) Values calculated with the atomic coordinates in the reference. c) Photographic data. d) phen=1,10-Phenanthroline and pydca =pyridine-2,6-dicarboxylate.

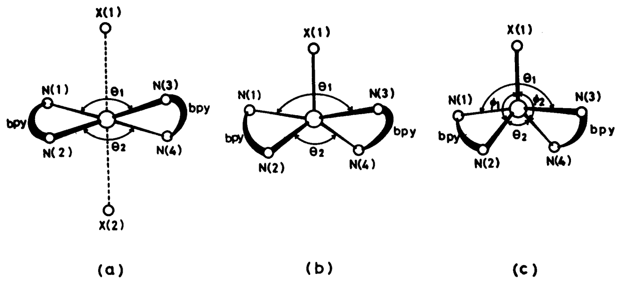


Fig. 3. Structures of bis(bipyridine)copper(II) complexes and their numbering schemes. (a): Distorted *trans*-octahedral structure ((1)—(4) complexes in Table 4), (b): five-coordinate structure with $\theta_1 < 180°$ ((5)—(8) complexes in Table 4), (c): five-coordinate structure with $\theta_1 > 180°$ ((9)—(15) complexes in Table 4).

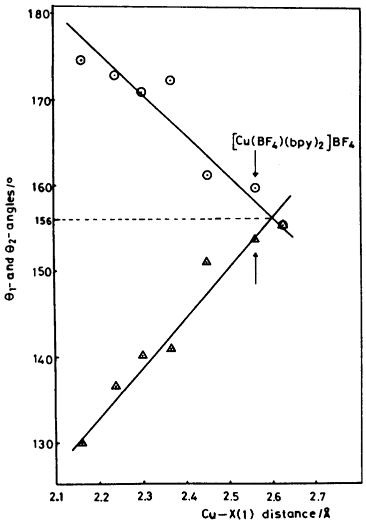


Fig. 4. Correlation between the Cu-X(1) distances (X=O or F) and the angles of θ_1 (⊙) and θ_2 (△) in the (2)—(8) complexes of Table 4. The values denoted by ⊙ and △ line up from right to left in numerical order respectively.

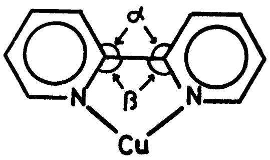
and [CuX(bpy)$_2$] (X=S_3O_6[9] and S_4O_6[10]).

For comparison, the main bond lengths and angles around the copper atom are given in Table 4; those for [Cu(S_3O_6)(bpy)$_2$] have not yet been reported in detail. In three *trans*-octahedral complexes (except [Cu(S_3O_6)(bpy)$_2$]), it is very interesting that as the axial Cu–X(1) distances (X=O or F) decrease from 2.627(6) Å in [Cu(S_4O_6)(bpy)$_2$][10] to 2.566(6) Å in the present complex and to 2.45(2) Å in [Cu(ClO_4)(bpy)$_2$]ClO_4,[8] the θ_1-angles increase from 155.2° to 161.1(8)° and the θ_2-angles decrease from 155.2° to 151.0(7)° systematically. On the other hand, the distances between the X(1) and the N(1) (or N(3)) atoms in those complexes are 2.91, 2.949(8), and 2.79(3) Å respectively; these values are approximately equal to the sum of the van der Waals radii of O(or F) and N atoms. These prove that the enlargement of the θ_1-value with the decrease of the Cu–X(1) distance is due to the steric interference between the X(1) atom and the atoms of N(1) and N(3) in the flattened tetrahedral Cu(bpy)$_2$-moiety. Similar correlations between the Cu–O(1) distances and the angles of θ_1 and θ_2 have also been found in [CuN_4O]-chromophores of bis(bipyridine)copper(II) complexes, having θ_1-values<180° (Table 4). The plots of the θ_1- and θ_2-angles against the Cu–X(1) distances (X=O or F) in the complexes mentioned above are shown in Fig. 4 and have been found to be linear. As a result, the θ_1-angle is expected to become 180° when the Cu–X(1) distance is about 2.1 Å; on the other hand, in the complexes of (9)—(15) of Table 4 with Cu–X(1) distances(X=N or O)<2.1 Å and θ_1-angles>180°, a great lengthening has been observed in the Cu–N(4) distance from 2.1 Å to 2.2 Å, and, as has been suggested by Hathaway,[2,6] the angle of X(1)–Cu–N(2) (=ϕ_1 in Fig. 3), which is opposite the Cu–N(4) bond, is considered to play an important role in the decision of their stereochemistries.

Table 5. Deviations of atoms from least-squares planes and dihedral angles

Deviations (l/Å) of atoms from the planes					
(A) Pyridine ring I					
N(1)	0.023	C(1)	−0.012	C(2)	−0.007
C(3)	0.014	C(4)	−0.005	C(5)	−0.013
(B) Pyridine ring II					
N(2)	−0.011	C(6)	0.006	C(7)	0.001
C(8)	−0.003	C(9)	−0.002	C(10)	0.009
(C) Bipyridine ligand I					
N(1)	0.076	C(1)	0.010	C(2)	−0.033
C(4)	−0.016	C(5)	0.024	C(6)	0.005
C(6)	0.005	C(7)	0.025	C(8)	0.018
C(9)	−0.011	C(10)	−0.025	N(2)	−0.041
(D) Pyridine ring III					
N(3)	0.004	C(11)	−0.006	C(12)	0.004
C(13)	0.001	C(14)	−0.003	C(15)	0.001
(E) Pyridine ring IV					
N(4)	−0.012	C(16)	0.002	C(17)	0.007
C(18)	−0.005	C(19)	−0.005	C(20)	0.014
(F) Bipyridine ring II					
N(3)	0.117	C(11)	0.105	C(12)	0.009
C(13)	−0.099	C(14)	−0.102	C(15)	0.010
C(16)	−0.006	C(17)	0.110	C(18)	0.100
C(19)	−0.006	C(20)	−0.096	N(4)	−0.124
(G) Plane through Cu, N(1), N(2), N(3), and N(4)					
Cu	−0.016	N(1)	−0.511	N(2)	0.445
N(3)	−0.216	N(4)	0.430		
Dihedral angles (ϕ/°) between the planes					
(A)-(B)	3.1	(D)-(E)	10.2	(C)-(F)	44.5

The bipyridine ligands are not planar, but the pyridine rings are planar within ±0.023 Å. The pyridine rings of the bipyridine molecule are slightly twisted from each other about the 2,2′-carbon bond; the twist angle is 3.1° for the molecule comprising N(1) and N(2) and 10.2° for the other, values of which are in the range of 0.1—13° reported previously.[5,8] Furthermore, the bond angle of α is larger than that of β by 7.9—9.2°. A



similar difference in these angles (5—10°) has also been observed in the crystal structure of the 2,2′-bipyridine molecule[18] and its copper(II) complexes.[8] Bond lengths and angles in bipyridine ligands are in good agreement with the previously reported ones.[4]

The B–F bond lengths and F–B–F angles of bridging BF_4^- ions are in the range of 1.359(9)—1.394(9) Å and 108.1(6)—110.8(6)° respectively, while those of the uncoordinating BF_4^- anions are less accurate and can not be discussed in detail because of the distorted arrangement in the crystal. The closest approach of the uncoordinating BF_4^- ion to the bipyridine ligand is 3.23(2) Å, between the F(22) and C(3)[$1-x$, $1-y$, $1-z$] positions.

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