The Crystal Structure of Perchlorato-bis(2,2′-bipyridine)-copper(II) Perchlorate, $[Cu(ClO_4)(bipy)_2]ClO_4$

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The structure of bis(2,2′-bipyridine)copper(II) perchlorate, $Cu(bipy)_2(ClO_4)_2$, has been determined from three-dimensional X-ray data collected by the photographic method. The compound forms triclinic crystals with $a=7.44(1)$, $b=14.93(1)$, $c=15.32(1)$ Å, $\alpha=136.3(0.1)$, $\beta=103.7(0.1)$, $\gamma=83.2(0.1)°$, and $Z=2$ in the space group $P\bar{1}$. The structure was solved by the usual Patterson and Fourier techniques and was refined by the least-squares method to an R value of 0.134. The crystal is composed of an infinite chain of $[Cu(ClO_4)(bipy)_2^+]_\infty$ and ClO_4^-; a perchlorate ion in the chain bridges two adjacent copper atoms through its two oxygen atoms. Roughly speaking, the coordination polyhedron around the copper atom is a tetragonally-distorted octahedron; the four nitrogen atoms of bipyridine molecules are arranged in a flattened tetrahedral manner (average Cu–N=1.99 Å), the least-squares plane of these atoms making an equatorial plane, while the polar positions are occupied by the two oxygen atoms of perchlorate anions, the Cu–O distances being 2.45 and 2.73 Å. The two pyridine rings are twisted slightly to each other in both of the bipyridine molecules; the dihedral angle between the pyridine planes is 13° in one bipyridine ligand and 4° in the other.

It is well known that the copper(II) ion can give numerous bis-bipyridine complexes with the general formula of $Cu(bipy)_2X_2\cdot nH_2O$.[1] In these complexes, however, two bipyridine molecules have to overcome a great difficulty; in case they take a completely coplanar arrangement around the Cu atom, there is severe steric interference between the hydrogen atoms on the 6- and 6′-carbon atoms of the two bipyridine molecules (Fig. 1). In fact, no such coplanar disposition of bipyridine molecules has been found for the bis-bipyridine metal complexes, including even the copper(II) complexes,[2-4] in which the bipyridine molecules are most likely to be on a plane.

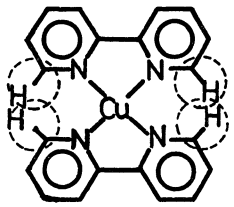


Fig. 1

The author has been very interested in the structure of bipyridine-copper(II) complexes, and has been attempting the crystal-structure analyses of a series of bis-bipyridine complexes in order to elucidate the disposition of the two bipyridine ligands around the copper(II) ion as well as the conformation of the bipyridine molecule in the complex. One of the results ($[Cu(NO_3)(bipy)_2]NO_3\cdot H_2O$) has already been reported briefly.[3] In this paper, the crystal structure of $Cu(bipy)_2(ClO_4)_2$ will be dealt with.

Experimental

The crystals of $Cu(bipy)_2(ClO_4)_2$ were prepared by Jaeger's method[5] and were recrystallized from a water-methanol mixture.

The lattice constants at room temperature were determined from $(h0l)$, $(0kl)$, and $(hk0)$ reflection data recorded on Weissenberg photographs on which the aluminum powder diffraction lines were superimposed for calibration. Cu$K\alpha$ radiation ($\lambda=1.5418$ Å) was used throughout the diffraction study. The density of the compound was determined by floatation in a benzene-bromoform mixture. Of the two possible triclinic space groups, $P\bar{1}$ and $P1$, the former was chosen initially; this choice was confirmed by the successful solution and refinement of the structure. The crystal data are listed in Table 1.

Table 1. Crystal data

$Cu(bipy)_2(ClO_4)_2$		
Triclinic		
$a=7.44\pm0.01$,	$b=14.93\pm0.01$,	$c=15.32\pm0.01$Å
$\alpha=136.3\pm0.1$,	$\beta=103.7\pm0.1$,	$\gamma=83.2\pm0.1°$
$Dm=1.68$ g/cm^3,	$Dc=1.69$ g/cm^3	
$Z=2$, Space group $P\bar{1}$		
Linear absorption coefficient for Cu$K\alpha$, $\mu=40.2$ cm^{-1}		

The intensity data of the $0kl$—$4kl$, $h0l$, and $hk0$ reflections were collected from crystals with dimensions of $0.15\times0.15\times1.0$ mm by the multiple-film equi-inclination techniques. The intensity scale was prepared from the same crystal and was used for the visual estimation of the 3064 independent reflcetions, but the intensities of 792 of them were too weak to be measured and so were assumed to be zero.

After the intensity data had been corrected for Lorentz-polarization effects and spot extension, the structure factors were placed on a common arbitrary scale by internal correlation. No absorption correction was made, for it was estimated that the maximum effect of absorption on the intensity was, at most, 15 per cent.

1) C. M. Harris, T. N. Locker, and H. Waterman, *Nature*, **192**, 424 (1961).

2) G. A. Barclay and C. H. L. Kennard, *ibid.*, **192**, 425 (1961); G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc., A*, **1963**, 5691.

3) H. Nakai, S. Ooi, and H. Kuroya, This Bulletin, **43**, 577 (1970).

4) I. M. Procter and F. S. Stephens, *J. Chem. Soc., A*, **1969**, 1248.

5) F. M. Jaeger and J. A. Dijk, *Z. Anorg. Chem.*, **227**, 273 (1936).

Structure Determination

The position of the copper atom was readily determined from the three-dimensional Patterson maps. A first Fourier synthesis, phased on the Cu atom, clearly gave the atomic positions of one bipyridine ligand and those of the coordinating ClO_4^- ion. The coordinates of the remaining non-hydrogen atoms were obtained from the subsequently-synthesized Fourier maps. In these diagrams, the electron-density distribution of the uncoordinating ClO_4^- ion was evidently indicative of its tetrahedral configuration, but was much more diffuse than that of the coordinating ClO_4^- anion. The crystal structure was refined by a block-diagonal least-squares method. Throughout the least-squares calculations, the following weighting scheme was employed:

$$w = 0.2, \text{ if } F_o \leq F_{\min} \ (= 0.5 = 0.01 \times F_{\max})$$

and

$$w = 1.0, \text{ if } F_{\min} < F_o.$$

The atomic scattering curves were taken from the International Tables for X-ray Crystallography, Vol. III,[6] the real part of the anomalous dispersion correction ($\Delta f' = -2.1$) being applied for the neutral copper atom. After three cycles of the refinements, the conventional R value was 0.17 for 2272 non-zero reflections. Three more cycles of the refinements with anisotropic thermal parameters for only the heavier atoms of Cu, Cl(1) and Cl(2) reduced the R value to 0.15. At this stage, the average isotropic temperature factor of the oxygen atoms of the uncoordinating ClO_4^- ion rose to 19 Å^2. In the further refinement, the anisotropic thermal parameters were introduced, in addition to the heavier atoms mentioned above, to the oxygen atoms of the uncoordinating ClO_4^- ion. The R value was improved to 0.134 by three cycles of the least-squares calculations. In the last cycle of the calculations, the maximum shift in any parameter was less than one-eighth of its estimated standard deviation. The final atomic coordinates and temperature factors are listed in Table 2.

Table 2 The atomic coordinates, thermal parameters, and their estimated standard deviations

ATOM	x	y	z	B(Å^2)
Cu	0.4174(4)	0.3636(2)	0.1304(2)	*
Cl(2)	0.175(1)	0.092(1)	0.369(1)	*
O(11)	0.183(6)	0.062(2)	0.436(2)	*
O(22)	0.083(5)	0.181(3)	0.388(3)	*
O(33)	0.353(3)	0.136(3)	0.412(3)	*
O(44)	0.173(3)	−0.025(2)	0.238(2)	*
Cl(1)	−0.0748(6)	0.3703(3)	0.1567(3)	*
O(1)	0.730(2)	0.321(1)	0.087(1)	7.4(3)
O(2)	0.934(2)	0.508(1)	0.267(1)	8.0(4)
O(3)	0.991(2)	0.314(1)	0.203(1)	6.9(3)
O(4′)	0.038(2)	0.336(1)	0.070(1)	5.8(3)
N(1)	0.356(2)	0.197(1)	0.069(1)	4.0(3)
C(1)	0.245(2)	0.097(2)	−0.043(2)	4.6(3)
C(2)	0.187(3)	−0.011(2)	−0.068(2)	5.9(4)
C(3)	0.251(3)	−0.010(2)	0.026(2)	6.1(4)
C(4)	0.370(3)	0.098(2)	0.142(2)	4.8(4)
C(5)	0.415(2)	0.201(2)	0.161(2)	4.5(3)
C(6)	0.539(2)	0.315(1)	0.278(1)	4.0(3)
C(7)	0.647(3)	0.320(1)	0.371(2)	4.9(4)
C(8)	0.759(3)	0.539(2)	0.496(2)	5.4(4)
C(9)	0.758(3)	0.435(2)	0.480(2)	5.7(4)
C(10)	0.651(2)	0.525(1)	0.396(1)	4.3(3)
N(2)	0.544(2)	0.416(1)	0.292(1)	3.8(3)
N(3)	0.345(2)	0.536(1)	0.196(1)	4.4(3)
C(11)	0.325(3)	0.638(2)	0.314(2)	5.8(4)
C(22)	0.245(3)	0.751(2)	0.350(2)	7.8(5)
C(33)	0.193(3)	0.743(2)	0.256(2)	8.8(6)
C(44)	0.205(3)	0.635(2)	0.128(2)	7.4(5)
C(55)	0.289(3)	0.524(2)	0.099(2)	5.4(4)
C(66)	0.312(3)	0.404(2)	−0.027(2)	5.5(4)
C(77)	0.271(3)	0.385(2)	−0.138(2)	7.6(5)
C(88)	0.305(3)	0.260(2)	−0.252(2)	8.5(6)
C(99)	0.381(3)	0.162(2)	−0.264(2)	7.5(5)
C(00)	0.415(3)	0.197(2)	−0.144(2)	6.5(5)
N(4)	0.377(2)	0.312(1)	−0.035(1)	5.0(3)

* Anisotropic thermal parameters ($\times 10^3$) with estimated standard deviations ($\times 10^3$) in parentheses. The expression of the anisotropic thermal parameters is $\exp[-(B_{11}\times h^2+B_{22}\times k^2+B_{33}\times l^2+B_{12}\times h\times k+B_{13}\times h\times l+B_{23}\times k\times l)]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	27(1)	11(0.2)	9(0.2)	1(1)	2(1)	15(0.4)
Cl(2)	79(3)	14(1)	12(1)	−10(2)	−9(2)	18(1)
O(11)	267(24)	34(4)	27(4)	11(16)	68(15)	50(7)
O(22)	152(16)	29(5)	58(7)	60(14)	54(17)	62(10)
O(33)	65(9)	54(6)	53(6)	−21(11)	−42(11)	78(11)
O(44)	98(9)	16(2)	15(2)	−8(7)	−7(7)	17(4)
Cl(1)	17(2)	10(0.2)	9(0.1)	3(0.4)	4(0.1)	15(1)

Results and Discussion

The crystal structure of $Cu(bipy)_2(ClO_4)_2$ viewed down the a-axis is shown in Fig. 2, while the bond lengths and angles, together with their estimated standard deviations, are presented in Table 3. The crystal is composed of the perchlorate ion and an infinite chain of $[Cu(ClO_4)(bipy)_2^+]_\infty$ in which a ClO_4^- ion bridges two adjacent copper atoms. A schematic drawing of a part of the infinite chain is shown in Fig. 3.

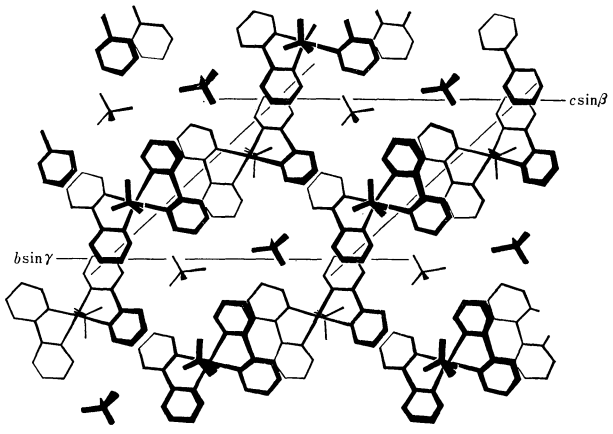


Fig. 2. a-axis projection of the crystal structure.

6) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

TABLE 3. BOND LENGTHS (Å) AND ANGLES (DEG) WITH ESTIMATED STANDARD DEVIATION IN PARENTHESES

Cu–N(1)=1.98(2)	Cu–N(2)=1.97(2)
Cu–N(3)=2.02(2)	Cu–N(4)=1.99(2)
Cu–O(1)=2.45(2)	Cu–O(4')=2.73(2)
N(1)–C(1)=1.33(3)	N(1)–C(5)=1.35(3)
C(1)–C(2)=1.45(4)	C(2)–C(3)=1.40(4)
C(3)–C(4)=1.41(4)	C(4)–C(5)=1.40(3)
C(5)–C(6)=1.46(3)	C(6)–C(7)=1.41(3)
C(7)–C(8)=1.40(3)	C(8)–C(9)=1.39(4)
C(9)–C(10)=1.42(3)	C(10)–N(2)=1.33(3)
C(6)–N(2)=1.37(3)	N(3)–C(11)=1.31(3)
N(3)–C(55)=1.34(3)	C(11)–C(22)=1.44(4)
C(22)–C(33)=1.32(5)	C(33)–C(44)=1.38(5)
C(44)–C(55)=1.46(4)	C(55)–C(66)=1.43(4)
C(66)–C(77)=1.47(4)	C(77)–C(88)=1.41(5)
C(88)–C(99)=1.39(5)	C(99)–C(00)=1.47(4)
C(00)–N(4)=1.34(3)	C(66)–N(4)=1.33(3)
Cl(1)–O(1)=1.48(2)	Cl(1)–O(2)=1.42(2)
Cl(1)–O(3)=1.42(2)	Cl(1)–O(4)=1.48(2)
Cl(2)–O(11)=1.37(4)	Cl(2)–O(22)=1.29(5)
Cl(2)–O(33)=1.33(4)	Cl(2)–O(44)=1.41(4)
N(1)–Cu–N(2)=83.8(0.7)	N(1)–Cu–N(3)=151.0(0.7)
N(1)–Cu–N(4)=102.0(0.8)	N(2)–Cu–N(3)=102.3(0.7)
N(2)-Cu–N(4)=161.1(0.8)	N(3)–Cu–N(4)=81.6(0.8)
O(1)–Cu–N(1)=98.0(0.7)	O(1)–Cu–N(2)=84.1(0.7)
O(1)–Cu–N(3)=110.7(0.7)	O(1)–Cu–N(4)=77.0(0.7)
O(4')–Cu–N(1)=75.5(0.6)	O(4')–Cu–N(2)=117.3(0.6)
O(4')–Cu–N(3)=76.6(0.6)	O(4')–Cu–N(4)=82.0(0.7)
O(1)–Cu–O(4')=156.2(0.6)	Cu–N(1)–C(1)=127(2)
Cu–N(2)–C(10)=127(1)	Cu–N(1)–C(5)=113(1)
Cu–N(2)–C(6)=112(1)	Cu–N(3)–C(11)=124(2)
Cu–N(4)–C(00)=124(2)	Cu–N(3)–C(55)=111(2)
Cu–N(4)–C(66)=114(2)	Cu–O(4')–Cl(1')=124(1)
Cu–O(1)–Cl(1)=140(1)	N(1)–C(1)–C(2)=122(2)
C(1)–C(2)–C(3)=119(2)	C(2)–C(3)–C(4)=118(2)
C(3)–C(4)–C(5)=120(2)	C(4)–C(5)–C(6)=124(2)
C(4)–C(5)–N(1)=122(2)	N(1)–C(5)–C(6)=114(2)
C(5)–C(6)–C(7)=122(2)	C(5)–C(6)–N(2)=116(2)
N(2)–C(6)–C(7)=122(2)	C(6)–C(7)–C(8)=117(2)
C(7)–C(8)–C(9)=121(2)	C(8)–C(9)–C(10)=119(2)
C(9)–C(10)–N(2)=120(2)	C(10)–N(2)–C(6)=121(2)
N(3)–C(11)–C(22)=122(2)	C(11)–C(22)–C(33)=115(3)
C(22)–C(33)–C(44)=125(3)	C(33)–C(44)–C(55)=116(3)
C(44)–C(55)–C(66)=125(2)	C(44)–C(55)–N(3)=117(2)
C(55)–C(66)–N(4)=115(2)	N(3)–C(55)–C(66)=118(2)
C(55)–C(66)–C(77)=122(2)	C(66)–C(77)–C(88)=113(3)
C(77)–C(88)–C(99)=127(3)	C(77)–C(66)–N(4)=123(2)
C(88)–C(99)–C(00)=114(3)	C(99)–C(00)–N(4)=122(2)
C(00)–N(4)–C(66)=122(2)	O(1)–Cl(1)–O(2)=109(1)
O(1)–Cl(1)–O(3)=108(1)	O(1)–Cl(1)–O(4)=110(1)
O(2)–Cl(1)–O(3)=108(1)	O(3)–Cl(1)–O(4)=110(1)
O(2)–Cl(1)–O(4)=111(1)	O(11)–Cl(2)–O(22)=126(3)
O(11)–Cl(2)–O(33)=97(3)	O(11)–Cl(2)–O(44)=108(2)
O(22)–Cl(2)–O(33)=105(3)	O(22)–Cl(2)–O(44)=116(2)
O(33)–Cl(2)–O(44)=101(2)	

TABLE 4. THE DEVIATIONS OF THE ATOMS FROM THE LEAST-SQUARES PLANES

(X, Y, and Z are coordinates in Å unit referred to an orthagonal set of axis, where Y is parallel to b and X lies in the (ab) plane.)

Best planes through pyridine rings			
0.882 X−0.266 Y−0.389 Z=1.56			
N(1)	−0.01 Å	C(3)	0.00 Å
C(1)	−0.01	C(4)	−0.01
C(2)	0.01	C(5)	0.02
0.883 X−0.052 Y−0.467 Z=1.72			
N(2)	0.00 Å	C(8)	−0.01 Å
C(6)	0.01	C(9)	0.02
C(7)	−0.01	C(10)	−0.01
0.923 X+0.319 Y+0.217 Z=4.87			
N(3)	−0.01 Å	C(33)	−0.02 Å
C(11)	0.01	C(44)	0.01
C(22)	0.00	C(55)	0.00
0.933 X+0.257 Y+0.251 Z=4.46			
N(4)	0.02 Å	C(88)	0.03 Å
C(66)	0.00	C(99)	−0.01
C(77)	−0.02	C(00)	−0.01
Plane formed by Cu, N(1), and N(2)			
0.929 X−0.151 Y−0.339 Z=1.98			
Plane formed by Cu, N(3), and N(4)			
0.962 X+0.168 Y+0.216 Z=4.11			
Best planes through bipyridine ligands			
0.890 X−0.154 Y−0.430 Z=1.67			
N(1)	−0.13 Å	N(2)	0.12 Å
C(1)	−0.14	C(6)	0.01
C(2)	0.02	C(7)	−0.15
C(3)	0.16	C(8)	−0.14
C(4)	0.15	C(9)	0.02
C(5)	0.04	C(10)	0.12
0.932 X+0.285 Y+0.224 Z=4.66			
N(3)	−0.06 Å	N(4)	0.08 Å
C(11)	−0.03	C(66)	0.02
C(22)	0.01	C(77)	−0.05
C(33)	0.02	C(88)	−0.02
C(44)	0.05	C(99)	−0.03
C(55)	−0.01	C(00)	0.03
Plane formed by N(1), N(2), N(3), and N(4)			
0.994 X+0.108 Y−0.008 Z=3.64			
N(1)	0.68 Å	N(3)	0.24 Å
N(2)	−0.37	N(4)	−0.36
Distance from the above plane			
Cu	−0.03 Å		

In the complex cation the two Cu–O bond lengths are not equal; one is 2.73 Å, and the other, 2.45 Å. It is worthy of note that these values are within the range of 2.2—2.9 Å, the range[7] which is known as the axial Cu–O distance in the tetragonally-distorted octahedral geometry of Cu(II). Four nitrogen atoms of the bipyridine ligands are arranged around the copper atom in a flattened tetrahedral manner (Cu–N= 1.99 Å on the average); the copper atom lies almost on the least-squares plane defined by these nitrogen atoms, and the Cu–O bonds are approximately normal to this plane. This is attributable to the steric interference between the chelating ligands; since the $Cu(bipy)_2^{2+}$ moiety, as has been stated in the introduction, can not have a strictly coplanar structure, the two bipyridine molecules are forced to slant against one another, giving rise to the tetrahedral arrangement of their

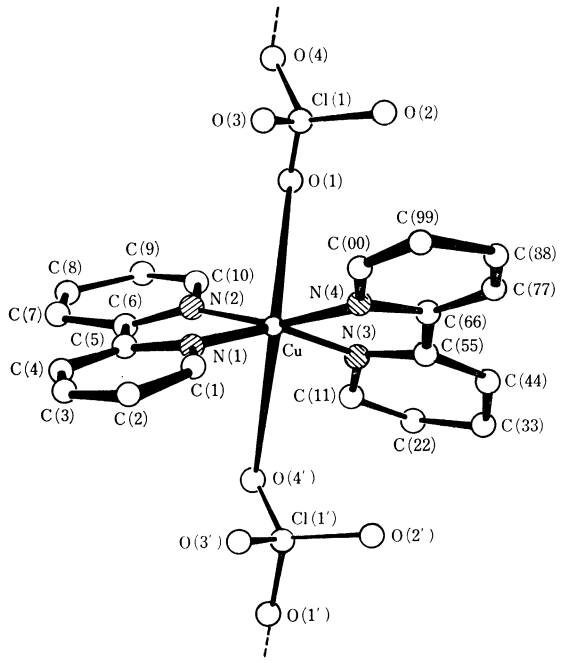


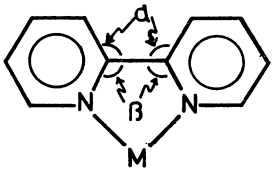
Fig. 3. A schematic drawing of a part of the infinite chain, $[Cu(ClO_4)(bipy)_2^+]_\infty$.

nitrogen atoms. The dihedral angle between the $Cu\lessdot^{N(1)}_{N(2)}$ and $Cu\lessdot^{N(3)}_{N(4)}$ planes is 37°.

As has been mentioned above, the axial Cu–O bonds are considerably longer than the Cu–N bonds; therefore, it is uncertain whether, in the strict sense, the oxygen atoms are in bonding with the copper atom or not. On the basis of the IR spectrum of $Cu(en)_2(ClO_4)_2$,[7] Hathaway and his coworkers inferred that the perchlorate anion is in "semi-coordination"[8] with the copper atom, irrespective of the Cu–O distance of 2.61 Å.[9] In the present compound, the distance of 2.45 Å between Cu and O(1) is significantly shorter than the Cu–O bond length in the ethylenediamine complex; hence, O(1) must be coordinated to Cu. Hathaway *et al.* investigated $Cu(bipy)_2(ClO_4)_2$, too. According to them, this compound gives a single broad reflectance band with a low intensity at 15.1×10^3 cm^{-1}, which is suggestive of a more tetragonally-distorted structure with an approximate center of symmetry, while it shows a single strong band at 1088 cm^{-1} and a weak band at 930 cm^{-1}, neigher of which is any evidence that ClO_4^- is coordinated or even semi-coordinated to Cu. Thus, they concluded that the compound should be formulated as $[Cu(bipy)_2](ClO_4)_2$ and that the complex cation has an essentially planar structure, although the two bipyridine ligands are twisted mutually by 10—30° towards a tetrahedral coordination This is not entirely in agreement with the result obtained in the present study regarding the aspect of the coordination of the ClO_4^- ion.

It should be remembered that the coexistence of the coordinating and uncoordinating ClO_4^- ions in the crystal would obscure the vibrational spectrum originating from the perchlorate anion and would make it difficult for them to establish the bonding feature of the anion. Considering such a situation as well as the presence of an approximate center of symmetry,[10] the present author should like to draw the following conclusion: having an appreciable influence on the chromophore $[CuN_4O(1)]$ with no center of symmetry, O(4') is possibly in "semi-coordination" with the copper atom, completing a distorted octahedron, though the Cu–O(4') distance is considerably longer than that of Cu–O(1). Thus, the complex could be regarded as hexa-coordinative.

The bipyridine ligands are not on a plane, but each individual pyridine ring is planar within the value of 0.03 Å. The pyridine rings of the bipyridine molecule are slightly twisted about the 2,2'-carbon bond by 13° and 4° for the molecules defined by N(1) and N(2) and by N(3) and N(4) respectively. Furthermore, the bond angle of α (123°) is larger than that of β by 7°, on the average. Although this value is not highly significant in view of its standard deviation, a similar difference in these bond angles (5—10°) is also observed in the crystal structures of the 2,2'-bipyridine molecule[11] and the bis-bipyridine complexes.[2-4,12]



The average Cl–O bond length and O–Cl–O angle of the bridging ClO_4^- ion are 1.45 Å and 109.5° respectively, while those of the uncoordinating ClO_4^- anion are less accurate and can not be discussed in detail because of the distorted arrangement in the crystal lattice. The closest approach of the uncoordinating perchlorate ion to the bipyridine ligand is 3.25 Å between the O(11) and C(88) $[x, y, 1+z]$. This value is comparable with the O–C distance (3.24 Å) found in $[Cu(ONO)(bipy)_2]NO_3$.

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