Crystal and Molecular Structure of Chlorobis(2,2′-bipyridyl)copper(II) Chloride Hexahydrate

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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 0·064 for 1307 independent reflections. The complex crystallises in the orthorhombic space group *Pnan*, with dimensions $a = 14{\cdot}376 \pm 0{\cdot}027$, $b = 14{\cdot}833 \pm 0{\cdot}028$, $c = 23{\cdot}339 \pm 0{\cdot}061$ Å, and $Z = 8$. The cation has C_2 symmetry and the environment about the copper atom is trigonal bipyramidal. The trigonal plane is formed by a nitrogen atom from each bipyridyl ligand (Cu–N 2·08 Å, subtending an angle of 123° at Cu) and the chlorine atom (Cu–Cl 2·36 Å). The remaining two bipyridyl nitrogen atoms occupy axial positions (Cu–N 1·98 Å) and the direction between these two nitrogen atoms lies 11·5° from the normal to the trigonal plane. The cations pack in sheets perpendicular to c at $z = \frac{1}{4}$ and $\frac{3}{4}$. The anionic chlorine atom and the water molecules are disordered in the channels between the cation sheets.

THE solid-state visible absorption spectra of $[Cu(bipy)_2I]X$ ($X = I$ or ClO_4 and bipy = 2,2′-bipyridyl) are similar[1] and the crystal structure of the former complex has shown the presence of the five-co-ordinate $[Cu(bipy)_2I]^+$ cation,[2] in which the copper atom possesses a stereochemistry intermediate between trigonal-bipyramidal and square-based pyramidal. However, for the complexes $[Cu(bipy)_2Cl]X$ the solid-state visible absorption spectrum for $X = ClO_4$ is sufficiently different from the spectra for $X = Cl,6H_2O$ and PF_6,H_2O to suggest the possibility of the presence of different stereochemistries.[1]

The crystal structure of $[Cu(bipy)_2Cl]Cl,6H_2O$ was undertaken to determine the stereochemistry of the copper atom.

EXPERIMENTAL

Crystal Data.—$C_{20}H_{28}Cl_2CuN_4O_6$, $M = 554{\cdot}9$, Orthorhombic, $a = 14{\cdot}376 \pm 0{\cdot}027$, $b = 14{\cdot}833 \pm 0{\cdot}028$, $c = 23{\cdot}339 \pm 0{\cdot}061$ Å, $U = 4976{\cdot}8$ Å^3, $D_m = 1{\cdot}47$ (by flotation), $Z = 8$, $D_c = 1{\cdot}481$, $F(000) = 1864$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 11·6 cm^{-1}, for cell dimensions and intensity measurements. Systematic absences: $0kl$ if $k = 2n + 1$ or if $l = 2n + 1$, $h0l$ if $h = 2n + 1$, and $hk0$ if $h + k = 2n + 1$. Space group *Pban* (No. 50), *Pnan* (No. 52), or *Pcan* (No. 60).

The complex crystallises as blue elongated-hexagonal plates lying on the (001) face with the elongation parallel to a and pinacoids {110}, {$\bar{1}$10}, and {010}. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. Intensities were measured on a Philips PAILRED diffractometer by use of monochromatised Mo-K_α radiation. Each reflection in the 0—13kl layers, to a maximum angle of θ 20°, was recorded. 1307 Reflections gave counts for which $\sigma(I)/I < 0{\cdot}5$.[3] Intensities were corrected for Lorentz and polarisation effects, but no correction for extinction or absorption 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

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[1] E. D. McKenzie, Ph.D. Thesis, University of New South Wales, 1962.

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

[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.

and chlorine atoms being corrected for anomalous dispersion.

Structure Determination.—From the systematic absences observed there would appear to be a space group ambiguity. An earlier determination of the crystal data for this complex gives $a = 14{\cdot}85$, $b = 23{\cdot}6$, $c = 14{\cdot}27$ Å and the space group as *Pncn* (non-standard *Pnna*, No. 52).[6] These cell parameters are in good agreement with those of the present determination and the space group agrees with the second of the presently suggested possibilities.

The largest vector peaks in the three-dimensional Patterson synthesis occur on sections $W = 0$ and $\frac{1}{2}$ and two of these peaks, namely those at $\frac{1}{2},\frac{1}{2},0$ and $\sim\frac{1}{4},0,\frac{1}{2}$, have heights approaching two-thirds of that of the origin peak. A consistent set of heavy-atom vectors could not be found for the space group *Pban* and hence this space group was rejected. For the other two space groups, *Pcan* and *Pnan*, solutions for the heavy-atom vectors for the copper atom and the chlorine atom bonded to it could be obtained. Since the set of vectors to be used in either case is the same, the arrangement of these atoms in the two possible lattices is similar. Further, for the two space groups there is a common Harker line vector, namely that at $\frac{1}{2},\frac{1}{2},\frac{1}{2} + 2z$, and this corresponds to the peak at $\frac{1}{2},\frac{1}{2},0$ in the Patterson map. Since the height of this peak is very large it indicates that much of the scattering matter must lie about $z = \frac{1}{4}$ in either space group. Consider the effect of such a situation in one of these space groups, that is, for instance, take the general position at $x,y,\frac{1}{4}$ in the space group *Pnan*. Symmetry elements beyond that defined by the space group are produced (see Figure 1), in particular, a *c*-glide plane perpendicular to *a*. Further, by shifting the origin by $\frac{1}{4},\frac{1}{4},0$ we have the representation for *Pcan*. Such a situation would give rise to the absences observed for the $0kl$ reflections of the present structure.

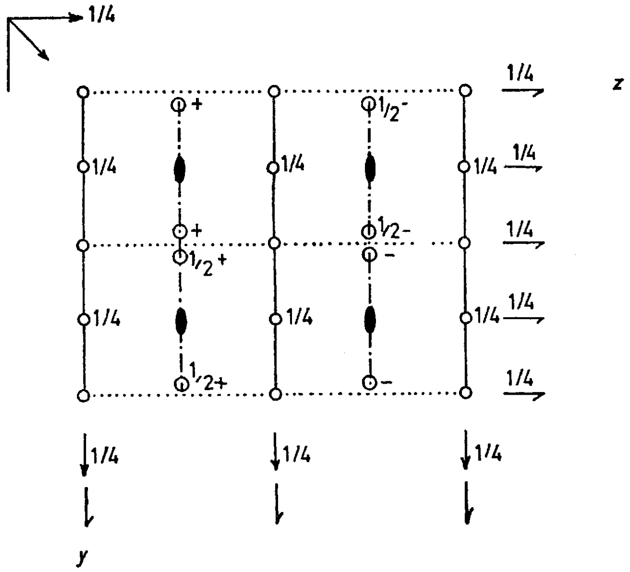

FIGURE 1 Representation of the space group *Pnan* with the general position at *x*, *y*, $\frac{1}{4}$. The extra symmetry elements are indicated by thick lines

Attempts to find a consistent solution from the Patterson synthesis for the second chlorine atom failed. Initially we chose to use the space group *Pcan* and a Fourier synthesis, phased on the copper and chlorine atoms, gave the positions of the two bipyridyl rings. Neither this Fourier synthesis nor a subsequent synthesis, phased on the increased number of atoms, yielded the position of the second chlorine atom. By use of the alternative space group, *Pnan*, the solution was similar to that obtained for *Pcan* with the origin shifted by $\frac{1}{4},\frac{1}{4},0$. This arrangement of the found $[Cu(bipy)_2Cl]^+$ cations, in either space group, produced sheets of ions perpendicular to *c* at $z = \frac{1}{4}$ and $\frac{3}{4}$. This arrangement defines channels between the sheets of ions, whose width projected down *a* is *ca.* 4·0 Å, centred about $z = 0$ and $\frac{1}{2}$ (see Figure 2). Difference-Fourier syntheses, phased on the atoms of the cation, showed many diffuse positive peaks in the region of the channels. We concluded therefore, that, provided the solution of the structure for the cation was correct, the structure was probably disordered in respect to the remaining chlorine atom and the water molecules, these atoms being randomly distributed in the channels.

At about this stage in the work our attention was brought to results of more recent preparations of this complex. In particular, it had been noted that chlorine-deficient samples had been obtained and in these cases chloride ion had been replaced by hydroxide ion.[7] Although originally satisfactory analyses for the complex had been obtained, a redetermination of the chlorine content was carried out on the sample from which the crystal used for the data collection was taken. This confirmed the presence of two chlorine atoms per copper atom [Cl: calc. 12·8, found 13·7%].

Since the solutions obtained so far by use of the two space groups were the same, the positions in one being related to those in the other by a shift of origin of $\frac{1}{4},\frac{1}{4},0$, it would seem likely that the structure as a whole would be the same by use of either space group with the provision of the change of origin. Thus from this point onwards in the work the space group *Pnan* was assumed and used.

Even though the solution obtained so far seemed most reasonable we felt it necessary to confirm or refute this solution particularly since we were unable to locate the second chlorine atom. We chose to use the symbolic addition method. From the 239 E values with $E > 1{\cdot}5$ the triple products were formed. The signs of 130 E values were determined, in terms of one symbol, using no relationship with a probability $<0{\cdot}96$. The choice of sign for this symbol, namely positive, was such to produce approximately equal numbers of E values with either sign. The E map calculated showed only two strong peaks, the larger being the copper atom. A Fourier synthesis, phased on these atoms, yielded a solution consistent with that found from the Patterson and Fourier syntheses. Thus we concluded that our earlier supposition that the structure was disordered in the channels was correct. The larger peaks in the difference Fourier syntheses, phase on the atoms of the cation, were assigned as oxygen atoms and included in subsequent calculations with B 9·0 Å^2.

Refinement of the structure was carried out by use of a least-squares procedure in which the function minimised was $\Sigma w\Delta^2$. The weight for each reflection, w, was unity for the initial refinement and was calculated from the expression $w = (10{\cdot}0 - 0{\cdot}04|F_o| + 0{\cdot}002|F_o|^2)^{-1}$ for the final refinement. For this latter weighting scheme the average values of $w\Delta^2$ for ranges of increasing $|F_o|$ were

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[6] D. E. C. Corbridge, Ph.D. Thesis, Leeds, 1951.

[7] E. D. McKenzie, personal communication.

almost constant. Reflections, whose calculated structure factors were less than one-third of the observed values, were omitted from the least-square analysis.

The initial refinement used a full-matrix technique in which the positional and individual isotropic thermal parameters of each atom of the cation were refined. The contribution of the hydrogen atoms of the bipyridyl rings was included, the positions of the hydrogen atoms being calculated from the ring geometry assuming C–H 1·00 Å. When the maximum shift in any parameter was of the order of its estimated standard deviation a further difference-Fourier synthesis was calculated. The map indicated the structure to be essentially correct. The region about the channels in the map showed that contributions from the oxygen atoms already included might be better interpreted in terms of partial occupancy and also showed further peaks which could be assigned as atoms with partial occupancy. From a series of difference maps, in which the number of atoms in the channels was varied, a total of fifteen atom positions was found to account for the electron density in the channels. Two of these positions were assigned as chlorine atoms with half occupancy on the basis of the contact distances. To test the correctness of the deduced structure the structure factors were calculated for the observed systematically absent $0kl$ reflections which are not a requirement of the space group, namely those for which $k + l = 2n$ and $k(l) = 2n + 1$. These reflections showed a general pattern of low magnitudes thus supporting the proposed structure.

The final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms of the cation and occupancy, positional, and individual thermal parameters for the atoms in the channel. However, owing to the large number of parameters to be refined (304) it was necessary to refine the parameters in a number of matrices; matrix (1) contained the overall scale and thermal parameter, matrix (2) the copper and chlorine atom of the cation, matrices (3) and (4) each bipyridyl ligand, matrix (5) the two chlorine atoms in the channels, and matrices (6)—(18) each oxygen atom of the channels. The refinement was terminated when the maximum shift in any parameter was $<0·16\ \sigma$, the shifts for any parameter of the cation were very much less than this value. 1285 reflections were included in the final cycle of refinement. The final values of R, based on 1307 reflections, and R' [$= \Sigma w\Delta^2/\Sigma w|F_o|^2$] were 0·064 and 0·006 respectively. A final difference-Fourier synthesis showed no peaks whose absolute density was $>0·5$ eÅ^{-3}.

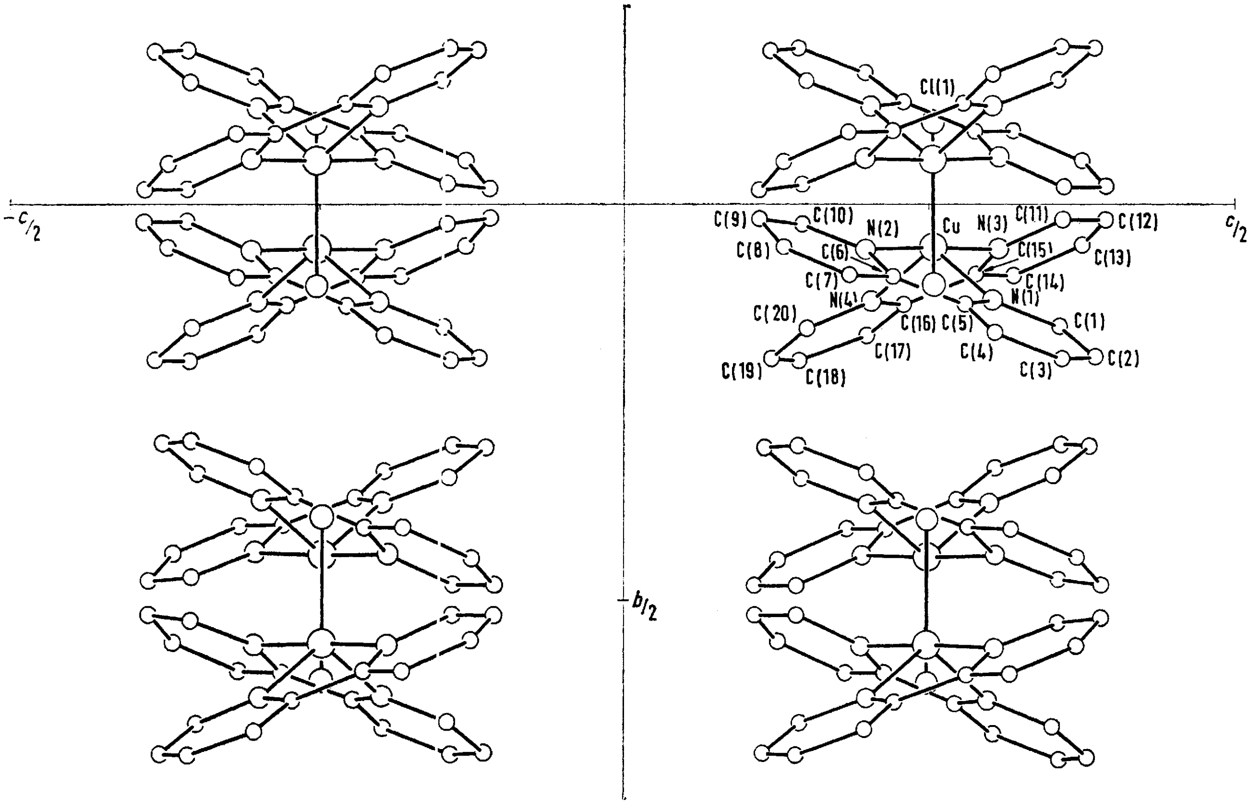

FIGURE 2 The packing of the $[Cu(bipy)_2Cl]^+$ cations in the crystal and the labelling of the atoms

Final atomic co-ordinates and thermal parameters for the cation are given in Tables 1 and 2, respectively. Table 3 gives the atomic co-ordinates, thermal parameters, and occupancy for the atoms in the channels. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20794 (9 pp., 1 microfiche).*

The calculations for the structure analysis were carried out on an Atlas computer at S.R.C., Chilton, and in the final stages on a PDP 10 at the University of Essex. The programmes used on the former computer were those of Hodgson, Mills, and Stephens and the Phase and Sigma 2

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

links of the '*X*-Ray '63' package. On the latter computer the programmes were those written by F. S. S. based on the Atlas programmes of Hodgson, Mills, and Stephens.

DISCUSSION

Since our interest in the structure lay solely with the cation no attempt will be made to discuss the atoms in the channels particularly as there appears to be considerable disorder in these channels. Table 4 gives the bond lengths and angles within the cation together with their estimated standard deviations derived directly from the least-squares inverse matrices. Figure 2 shows the packing of the cations in the crystal together with the labelling of these atoms.

TABLE 1

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

	x/a	y/b	z/c	δ_{rms}(Å)
Cu	−0·1118(1)	0·0559(1)	0·2517(1)	0·0016
Cl(1)	−0·1126(2)	−0·1032(2)	0·2513(2)	0·004
N(1)	−0·0124(7)	0·1224(7)	0·3005(4)	0·010
N(2)	−0·0053(8)	0·0578(8)	0·1973(4)	0·011
N(3)	−0·2175(8)	0·0581(7)	0·3054(4)	0·010
N(4)	−0·2102(8)	0·1239(7)	0·2021(5)	0·011
C(1)	−0·0224(11)	0·1554(9)	0·3544(6)	0·014
C(2)	0·0518(11)	0·1933(9)	0·3837(6)	0·014
C(3)	0·1368(10)	0·1959(9)	0·3576(7)	0·015
C(4)	0·1480(9)	0·1624(9)	0·3025(6)	0·014
C(5)	0·0727(11)	0·1270(8)	0·2767(5)	0·013
C(6)	0·0757(12)	0·0925(9)	0·2188(6)	0·016
C(7)	0·1554(10)	0·0904(9)	0·1836(6)	0·014
C(8)	0·1504(12)	0·0548(11)	0·1296(6)	0·016
C(9)	0·0695(13)	0·0203(10)	0·1093(5)	0·015
C(10)	−0·0096(9)	0·0229(9)	0·1446(6)	0·014
C(11)	−0·2168(11)	0·0203(10)	0·3581(5)	0·014
C(12)	−0·2945(12)	0·0196(10)	0·3929(5)	0·015
C(13)	−0·3790(9)	0·0522(10)	0·3729(6)	0·013
C(14)	−0·3805(8)	0·0900(9)	0·3175(6)	0·013
C(15)	−0·2992(10)	0·0907(7)	0·2861(5)	0·012
C(16)	−0·2928(11)	0·1284(8)	0·2274(5)	0·013
C(17)	−0·3706(9)	0·1663(9)	0·1987(7)	0·014
C(18)	−0·3602(10)	0·1981(10)	0·1434(6)	0·014
C(19)	−0·2731(12)	0·1956(9)	0·1193(5)	0·014
C(20)	−0·1993(9)	0·1576(10)	0·1497(7)	0·014
H(1)	−0·085	0·156	0·373	
H(2)	0·045	0·217	0·423	
H(3)	0·192	0·221	0·379	
H(4)	0·211	0·167	0·282	
H(7)	0·219	0·117	0·198	
H(8)	0·209	0·051	0·103	
H(9)	0·069	−0·006	0·070	
H(10)	−0·072	−0·004	0·131	
H(11)	−0·153	−0·006	0·371	
H(12)	−0·295	0·001	0·434	
H(13)	−0·432	0·044	0·401	
H(14)	−0·438	0·116	0·301	
H(17)	−0·430	0·168	0·219	
H(18)	−0·409	0·221	0·116	
H(19)	−0·265	0·223	0·081	
H(20)	−0·134	0·152	0·130	

The $[Cu(bipy)_2Cl]^+$ ion has approximately C_2 symmetry, the direction of the C_2 axis being collinear with the Cu–Cl(1) direction. Each bipyridyl ligand acts as a bidentate chelate through the nitrogen atoms, and a chlorine atom completes the five-co-ordination about the copper atom. The environment about the copper atom is approximately trigonal bipyramidal, the N(2) · · · N(3) direction lying 11·5° 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 1·98 and 2·08 Å, respectively. The two shorter Cu–N bonds are collinear, and the remaining two subtend an angle of 123° at the copper atom. The internal bipyridyl nitrogens subtend an angle of 79·5°. This arrangement of the bipyridyl ligands about the copper atom resembles the corresponding arrangements found in $[Cu(bipy)_2I]I$,[2]

TABLE 2

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

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	61·0(8)	73·2(8)	16·1(3)	1·5(8)	6·7(5)	0·5(7)
Cl(1)	58(2)	66(2)	36(1)	0(2)	10(1)	−2(2)
N(1)	60(7)	57(6)	10(2)	24(5)	9(3)	0(3)
N(2)	85(9)	59(7)	15(3)	9(6)	5(4)	−6(4)
N(3)	69(8)	67(7)	15(2)	−3(6)	−1(3)	2(4)
N(4)	73(8)	55(7)	17(3)	4(6)	10(4)	−4(3)
C(1)	111(13)	47(8)	18(3)	9(8)	12(5)	−6(4)
C(2)	85(11)	48(9)	23(3)	3(8)	−10(7)	−1(4)
C(3)	65(10)	48(8)	31(5)	−16(7)	−8(5)	10(5)
C(4)	59(9)	65(8)	17(3)	2(7)	0(4)	12(4)
C(5)	65(10)	52(8)	14(3)	12(7)	1(5)	−4(4)
C(6)	94(12)	51(8)	16(3)	4(8)	8(6)	7(4)
C(7)	93(11)	52(9)	21(4)	25(8)	10(5)	−1(4)
C(8)	105(12)	63(9)	20(4)	14(9)	13(5)	9(5)
C(9)	109(12)	70(10)	16(3)	14(9)	7(6)	−5(4)
C(10)	68(9)	60(9)	23(4)	7(7)	3(5)	0(4)
C(11)	122(13)	68(9)	14(3)	−4(8)	7(5)	7(4)
C(12)	93(11)	85(10)	18(3)	−18(9)	19(5)	−10(4)
C(13)	51(9)	63(8)	25(4)	−16(7)	16(4)	−11(5)
C(14)	42(8)	73(9)	19(3)	1(6)	15(4)	−10(4)
C(15)	62(9)	35(7)	14(3)	−12(6)	6(5)	−3(3)
C(16)	66(9)	33(6)	19(3)	15(6)	− 4(5)	−11(4)
C(17)	65(9)	42(7)	29(4)	−5(7)	5(5)	−13(5)
C(18)	69(10)	74(9)	20(4)	2(7)	−3(5)	−10(5)
C(19)	107(12)	54(8)	17(3)	7(8)	2(6)	6(4)
C(20)	65(9)	58(9)	26(4)	−3(7)	4(5)	−5(5)

For all hydrogen atoms $B = 6{\cdot}2$ Å². Anisotropic thermal parameters are given by: $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.

TABLE 3

Atomic co-ordinates (fractional), thermal parameters, and occupancy with estimated standard deviations in parentheses for the atoms in the channels

	Occupancy	x/a	y/b	z/c	B/Å²
Cl(2)	0·58(2)	0·8483(7)	0·1610(8)	0·4854(5)	12·5(5)
Cl(3)	0·49(2)	0·9265(10)	0·1665(10)	0·0142(6)	13·4(6)
O(1)	0·81(3)	0·4392(11)	0·0195(10)	0·4757(6)	10·5(7)
O(2)	0·28(3)	0·3614(22)	0·0384(23)	0·0330(14)	6·8(14)
O(3)	0·09(2)	−0·1268(36)	0·0881(36)	0·0209(23)	0·9(20)
O(4)	0·75(3)	0·8287(10)	0·0212(10)	0·0297(6)	9·2(6)
O(5)	0·52(3)	0·2962(20)	0·1688(22)	0·4851(14)	15·6(15)
O(6)	1·11(5)	0·3910(13)	0·1504(14)	0·0408(9)	20·5(11)
O(7)	0·78(5)	0·4043(21)	0·2272(24)	0·3663(14)	23·6(19)
O(8)	0·79(6)	0·3807(22)	0·1089(26)	0·4606(17)	26·6(24)
O(9)	0·19(2)	0	0·50	0	4·7(10)
O(10)	0·21(2)	−0·25	0·0296(24)	0	8·3(14)
O(11)	0·39(4)	0·3756(35)	0·2217(38)	0·1433(23)	19·5(30)
O(12)	0·26(3)	0·5221(35)	0·1794(38)	0·0097(23)	12·2(24)
O(13)	0·31(4)	0·25	0·2712(75)	0·25	39·4(65)

TABLE 4

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for the cation

(*a*) Distances

Cu–Cl(1)	2·361(4)	Cu–N(2)	1·989(10)
Cu–N(1)	2·077(10)	Cu–N(3)	1·970(10)
Cu–N(4)	2·087(11)		
N(1)–C(1)	1·358(15)	N(3)–C(11)	1·351(15)
C(1)–C(2)	1·386(18)	C(11)–C(12)	1·380(18)
C(2)–C(3)	1·367(18)	C(12)–C(13)	1·388(18)
C(3)–C(4)	1·387(18)	C(13)–C(14)	1·411(18)
C(4)–C(5)	1·346(17)	C(14)–C(15)	1·380(15)
C(5)–N(1)	1·344(15)	C(15)–N(3)	1·349(15)
C(5)–C(6)	1·447(17)	C(15)–C(16)	1·482(15)
C(6)–C(7)	1·409(19)	C(16)–C(17)	1·420(17)
C(7)–C(8)	1·368(19)	C(17)–C(18)	1·383(18)
C(8)–C(9)	1·357(20)	C(18)–C(19)	1·372(18)
C(9)–C(10)	1·405(18)	C(19)–C(20)	1·395(18)
C(10)–N(2)	1·335(16)	C(20)–N(4)	1·332(16)
N(2)–C(6)	1·369(17)	N(4)–C(16)	1·328(15)

(*b*) Angles

Cl(1)–Cu–N(1)	118·7(3)	Cl(1)–Cu–N(3)	90·9(3)
Cl(1)–Cu–N(4)	118·6(3)	N(1)–Cu–N(3)	100·0(4)
N(1)–Cu–N(4)	122·8(4)	N(4)–Cu–N(2)	99·3(5)
N(2)–Cu–N(3)	178·3(5)	N(1)–Cu–N(2)	79·3(4)
Cl(1)–Cu–N(2)	90·9(3)	N(3)–Cu–N(4)	79·8(4)
Cu–N(1)–C(1)	127·4(10)	Cu–N(3)–C(11)	124·6(10)
Cu–N(1)–C(5)	115·1(8)	Cu–N(3)–C(15)	117·7(8)
C(5)–N(1)–C(1)	117·4(12)	C(15)–N(3)–C(11)	117·4(11)
N(1)–C(1)–C(2)	121·5(13)	N(3)–C(11)–C(12)	122·1(14)
C(1)–C(2)–C(3)	118·6(13)	C(11)–C(12)–C(13)	120·6(13)
C(2)–C(3)–C(4)	120·4(12)	C(12)–C(13)–C(14)	117·3(11)
C(3)–C(4)–C(5)	117·5(12)	C(13)–C(14)–C(15)	118·5(12)
C(4)–C(5)–N(1)	124·6(12)	C(14)–C(15)–N(3)	123·9(11)
C(6)–C(5)–N(1)	113·3(14)	C(16)–C(15)–N(3)	113·0(12)
C(4)–C(5)–C(6)	122·1(16)	C(14)–C(15)–C(16)	123·1(14)
C(5)–C(6)–C(7)	125·2(17)	C(15)–C(16)–C(17)	122·5(15)
C(5)–C(6)–N(2)	116·7(14)	C(15)–C(16)–N(4)	116·6(13)
N(2)–C(6)–C(7)	118·1(13)	N(4)–C(16)–C(17)	121·0(12)
C(6)–C(7)–C(8)	120·2(15)	C(16)–C(17)–C(18)	119·3(12)
C(7)–C(8)–C(9)	120·8(14)	C(17)–C(18)–C(19)	118·2(13)
C(8)–C(9)–C(10)	118·6(12)	C(18)–C(19)–C(20)	119·8(12)
C(9)–C(10)–N(2)	120·9(13)	C(19)–C(20)–N(4)	121·9(13)
C(10)–N(2)–C(6)	121·5(11)	C(20)–N(4)–C(16)	119·7(12)
Cu–N(2)–C(6)	115·3(9)	Cu–N(4)–C(16)	112·6(9)
Cu–N(2)–C(10)	123·2(10)	Cu–N(4)–C(20)	127·7(10)

$[Cu(bipy)_2ONO]NO_3$,[8] and $[Cu(bipy)_2(NH_3)](BF_4)_2$.[9] However, in the present structure the angles subtended at the copper atom by the co-ordinating atoms in the trigonal plane show the least deviation from the expected value of 120°.

The bond lengths and angles within the bipyridyl ligands are in accordance with those previously reported.[2,8-10] The bipyridyl rings are planar within experimental error (see Table 5). This situation contrasts with that observed in other bis(bipyridyl)copper(II) complexes [2,8,9] in which the pyridyl rings are twisted about the 2,2′-bond by angles up to *ca.* 11°.

TABLE 5

Least-squares planes and their equation given by $lX + mY + nZ - p = 0$ where X, Y, and Z are co-ordinates in Å. Deviations (Å) of the most relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1)				
Bipyridyl ring N(1), N(2)	0·2320	−0·9009	0·3668	0·8939
[N(1) 0·002, C(1) −0·011, C(2) −0·020, C(3) 0·006, C(4) 0·019, C(5) 0·021, N(2) 0·006, C(6) −0·004, C(7) −0·012, C(8) −0·015, C(9) 0·002, C(10) 0·006, Cu 0·14]				
Plane (2):				
Bipyridyl ring N(3), N(4)	0·2264	0·8974	0·3787	2·7588
[N(3) 0·007, C(11) −0·029, C(12) 0·016, C(13) −0·002, C(14) 0·007, C(15) 0·002 N(4) −0·008, C(16) 0·007, C(17) 0·004, C(18) −0·028, C(19) 0·011, C(20) 0·013, Cu −0·15]				
Plane (3):				
Cu, Cl(1), N(1), N(4)	−0·6281	0·0034	0·7781	5·5771
[Cu 0·006, Cl(1) −0·002, N(1) −0·002, N(4) −0·002]				

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