A Structural Profile of the Bis(2,2'-bipyridyl)monochlorocopper(II) Cation. Crystal Structures of Bis(2,2'-bipyridyl)monochlorocopper(II) Perchlorate and the Nitrate Trihydrate

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The crystal structures of the title compounds $[Cu(bipy)_2Cl][ClO_4]$, (1), and $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$, (2), have been determined by *X*-ray diffraction methods using three-dimensional diffractometer data; the structures were solved by heavy-atom techniques and successive Fourier synthesis. Compound (1) crystallises in the monoclinic space group $P2_1/c$ with a = 10.761(5), b = 12.253(5), c = 16.990(5) Å, β = 112.18(5)°, Z = 4, and (2) crystallises in the monoclinic space group $P2_1/a$ with a = 14.305(5), b = 21.213(5), c = 8.234(5) Å, β = 114.90(4)°, Z = 4. The $[Cu(bipy)_2Cl]^+$ cation in both (1) and (2) involves a square-pyramidal distorted trigonal-bipyramidal CuN_4Cl chromophore with the distortion in (1) greater than in (2). From a correlation of the bond-length and bond-angle distortion of the structures of *five* $[Cu(bipy)_2Cl]^+$ cation distortion isomers a structural profile has been constructed between a near regular trigonal-bipyramidal CuN_4Cl chromophore of C_2 symmetry, and a square-pyramidal chromophore. The electronic reflectance spectra have been established as an 'electronic criteria of stereochemistry' for the CuN_4Cl chromophore, which involves a single peak at 12 500 cm^{-1} for the trigonal-bipyramidal geometry and twin peaks at 13 240 and 10 470 cm^{-1} for the square-pyramidal distorted structure.

THE lack of spherical symmetry of the copper(II) ion (d^9) is a major factor in the formation of non-regular stereochemistries in copper(II) complexes,[1,2] such as elongated tetragonal octahedral, in which the tetragonality[3] T(= mean in-plane copper–ligand bond distance divided by mean out-of-plane copper–ligand bond distance) is not fixed but variable over a limited range.[4,5] This implies that for the same set of ligands the eccentricity of the copper(II) ion prolate ellipsoid is also continuously variable[4] (within certain limits). The term 'plasticity' has been introduced[5] to describe this non-rigid property of the copper(II) ion in the stereochemistry of its complexes and has been used to justify the existence of its distortion isomers.[5,6] This term has recently been extended[7] to describe the existence of three cation distortion isomers, as in the five-co-ordinate structures of the $[Cu(dien)(bipyam)]^+$ cations (dien = diethylenetriamine and bipyam = 2,2'-bipyridylamine) or in the anion distortion isomers of the four-co-ordinate structures of the $[CuCl_4]^{2-}$ anions.[8,9] The individual structures in a series of distortion isomers (cation or anion) then represent individual points along a structural profile[10-12] which maps the change from one stereochemistry to another. The present paper describes a further series of cation distortion isomers, involving the five-co-ordinate bis(2,2'-bipyridyl)monochlorocopper(II) cation and describes the crystal structures of the two complexes bis(2,2'-bipyridyl)monochlorocopper(II) perchlorate, (1), and bis(2,2'-bipyridyl)monochlorocopper(II) nitrate trihydrate, (2).

EXPERIMENTAL

Preparations.—Both (1) and (2) were prepared by mixing 2,2'-bipyridyl (2.2 mol) in ethanol with 0.5 mol each of $CuCl_2\cdot 2H_2O$ and $[Cu(OH_2)_6][ClO_4]_2$ for (1) and 1.0 mol of $Cu[NO_3]_2\cdot 3H_2O$ for (2) in water and heating the solutions to boiling, filtering, and allowing the solutions to stand for a few days; both solutions yielded blue crystals of (1) and (2) respectively [(1) Found: C, 14.15; H, 3.10; Cl, 13.55; Cu, 12.15; N, 10.80. $C_{20}H_{16}Cl_2CuN_4O_4$ requires C, 14.05; H, 3.15; Cl, 13.90; Cu, 12.45; N, 10.95%. (2) Found: C, 46.70; H, 3.95; Cl, 7.45; Cu, 12.25; N, 13.40. $C_{20}H_{22}ClCuN_5O_6$ requires C, 47.15; H, 3.95; Cl, 6.95; Cu, 12.00; N, 13.75%].

Samples of bis[bis(2,2'-bipyridyl)monochlorocopper(II)] pentathionate hexahydrate[13] (3), bis(2,2'-bipyridyl)monochlorocopper(II) bis[dichlorocuprate(I)][14] (4), and bis(2,2'-bipyridyl)monochlorocopper(II) chloride hexahydrate[15-17] (5) were prepared as previously reported.

Crystallographic Data.—The initial space-group data were determined from precession photographs and refined on a Philips PW 1100 four-circle diffractometer using graphite monochromated Mo-K_α radiation. A θ—2θ scan mode was used and reflections with $3.0° < \theta < 30°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.7 + 0.1 \tan\theta)$ was used. With the acceptance criteria $I \geqslant 2.5\sigma(I)$, 2 761 unique reflections were retained for (1) and 3 264 for (2). Lorentz and polarisation corrections were applied but no correction was made for absorption. Both structures were solved using three-dimensional Patterson and Fourier techniques and refined by blocked-matrix least-squares analysis with anisotropic temperature factors for all the non-hydrogen atoms. The positions of the H atoms were calculated geometrically and floated on the positions of the adjacent C and O atoms, assuming a fixed C–H and O–H bond distance of 1.08 Å and a fixed temperature factor of 0.07 $Å^2$. Complex atomic scattering factors were used[18,19] and the copper atom was corrected for anomalous dispersion. All calculations were carried out using the programmes SHELX-76[20] and XANADU by G. M. Sheldrick, PLUTO by S. Motherwell, and XPUB by R. Taylor on an IBM 370/138 computer. Table 1 lists the crystal and refinement data for (1) and (2), Table 2 lists the final atom co-ordinates, Table 3 selected bond lengths, Table 4 selected bond angles, and Table 5 gives some selected relevant mean-planes data. Observed and calculated structure factors, calculated hydrogen-atom positions, anisotropic temperature factors, and full bond-

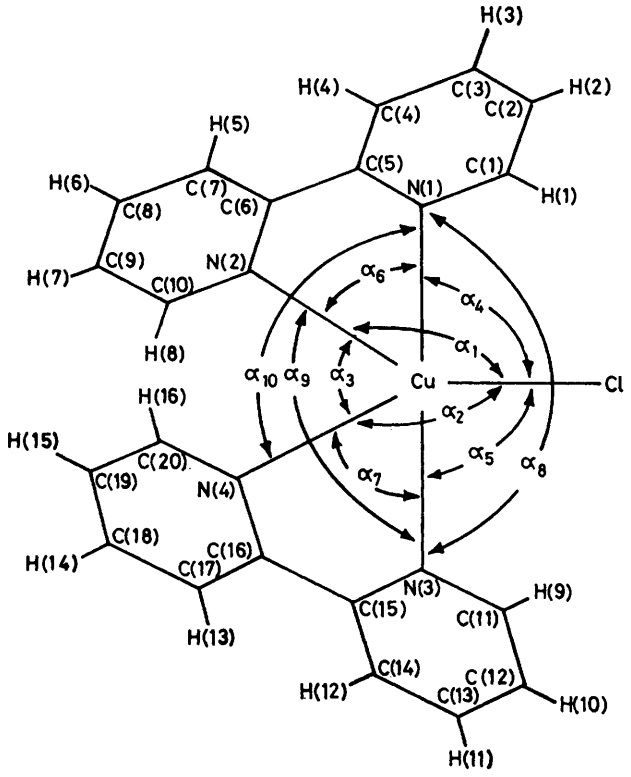


FIGURE 1 The molecular structure of the $[Cu(bipy)_2Cl]^+$ cation showing the atom numbering scheme and angle notation used

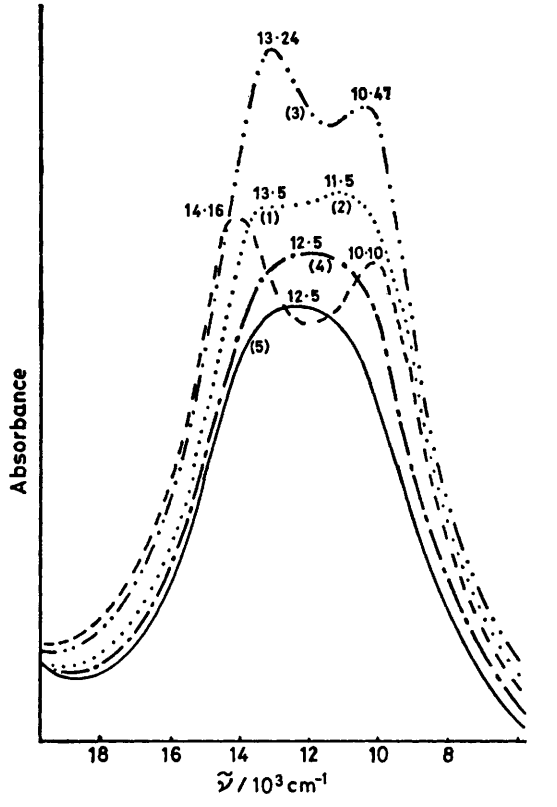


FIGURE 2 The electronic reflectance spectra of $[Cu(bipy)_2Cl]X$ (absorption maxima in 10^3 cm^{-1}): X = ClO_4 (1), $[NO_3]\cdot 3H_2O$ (2), $\frac{1}{2}\{[S_5O_6]\cdot 6H_2O\}$ (3), Cu^ICl_2 (4), and $Cl\cdot 6H_2O$(5)

length, bond-angle, and mean-planes data are in Supplementary Publication No. SUP 23057 (52 pp.).*

Figure 1 illustrates the overall molecular geometry of the $[Cu(bipy)_2Cl]^+$ cation, showing the atom numbering and angle notation used in (1) and (2). Table 6 summarises some relevant bond-distance and bond-angle data for the complexes (1)—(5).[13,14,17]

TABLE 1

Crystal and refinement data

	(1)	(2)
Compound	$[Cu(bipy)_2Cl][ClO_4]$	$[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$
M	509.45	529.00
Stoicheiometry	$C_{20}H_{16}Cl_2CuN_4O_4$	$C_{20}H_{22}ClCuN_5O_6$
Space group	$P2_1/c$	$P2_1/a$
a/Å	10.761(5)	14.305(5)
b/Å	12.253(5)	21.213(5)
c/Å	16.990(5)	8.234(5)
β/°	112.18(5)	114.90(4)
U/Å^3	2 074.36	2 266.28
Z	4	4
D_m (flotation)/ g cm^{-3}	1.616	1.581
D_c/g cm^{-3}	1.631	1.550
Radiation	Mo-K_α	Mo-K_α
$F(000)$	1 035.96	1 043.96
No. unique reflections	2 761	3 264
No. parameters varied	281	299
$R = (\Sigma\Delta/\Sigma\lvert F_o\rvert)$	0.038 7	0.054 6
$R' = (\Sigma\Delta w^{\frac{1}{2}}/\Sigma\lvert F_o\rvert w^{\frac{1}{2}})$	0.043 6	0.060 6
k	1.203 9	1.397 5
g	0.000 087	0.000 54
Max. final shift/e.s.d.*	0.06	0.03
Maximum residual electron density /e Å^{-3}	0.44	0.47
No. atom anisotropic	31	33
μ /cm^{-1}	12.91	10.80

* Estimated standard deviation.

Physical Properties.—The electronic reflectance spectra were recorded as previously reported [1,21] and are illustrated for the complexes (1)—(5) in Figure 2.

RESULTS AND DISCUSSION

The structures of both (1) and (2) involve $[Cu(bipy)_2Cl]^+$ cations, and perchlorate and nitrate anions, respectively. In (2), the water molecule is not involved in the co-ordination sphere of the copper(II) ion. The bond lengths and bond angles of the anions are consistent with a tetrahedral stereochemistry for the perchlorate anion,[22] and a trigonal-planar stereochemistry for the nitrate ion,[23] with no evidence for even semi-co-ordination [24] of these anions to the $[Cu(bipy)_2Cl]^+$ cations. The data for the bipy ligands (Tables 3 and 4) are consistent with the values previously reported; [25] the pyridine rings are planar (Table 5) and for each bipy ligand they are slightly inclined with respect to each other (Table 5) within the range 0—11°, as previously reported for the dihedral angle for this ligand.[26]

The $[Cu(bipy)_2Cl]^+$ cations of (1) and (2) both involve a five-co-ordinate CuN_4Cl chromophore with a distorted

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 2

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	(1) $[Cu(bipy)_2Cl][ClO_4]$			(2) $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Cu	1 300	445	3 626	2 545	−192	4 923(1)
Cl(1)	1 386(1)	−1 400(1)	3 607(1)	3 356(1)	75(1)	7 914(2)
N(1)	2 821(3)	558(2)	4 747(2)	3 315(3)	451(2)	4 211(5)
C(1)	2 972(3)	−95(3)	5 409(2)	3 396(4)	1 058(2)	4 696(7)
C(2)	4 089(4)	−40(4)	6 157(2)	3 952(4)	1 488(2)	4 231(7)
C(3)	5 077(4)	703(4)	6 207(3)	4 456(4)	1 290(3)	3 235(8)
C(4)	4 929(3)	1 375(3)	5 535(3)	4 393(3)	660(2)	2 719(7)
C(5)	3 779(3)	1 295(3)	4 805(2)	3 821(3)	244(2)	3 263(6)
C(6)	3 490(3)	1 990(3)	4 038(2)	3 711(3)	−437(2)	2 836(6)
C(7)	4 301(4)	2 833(3)	3 982(3)	4 169(3)	−732(3)	1 856(6)
C(8)	3 918(5)	3 431(3)	3 243(3)	4 004(4)	−1 380(3)	1 517(7)
C(9)	2 739(4)	3 194(3)	2 580(3)	3 379(4)	−1 694(3)	2 118(8)
C(10)	1 978(4)	2 339(3)	2 668(2)	2 962(4)	−1 370(2)	3 105(5)
N(2)	2 344(3)	1 740(2)	3 380(2)	3 113(3)	−756(2)	3 460(5)
N(3)	−232(3)	488(2)	2 507(2)	1 721(3)	−860(2)	5 408(5)
C(11)	−239(4)	−72(3)	1 821(2)	2 138(4)	−1 320(2)	6 583(7)
C(12)	−1 354(4)	−91(4)	1 067(2)	1 542(4)	−1 777(2)	6 927(8)
C(13)	−2 486(4)	460(3)	1 036(3)	494(4)	−1 743(2)	5 974(8)
C(14)	−2 486(3)	1 027(3)	1 728(2)	62(4)	−1 272(2)	4 759(7)
C(15)	−1 330(3)	1 037(3)	2 466(2)	685(3)	−823(2)	4 489(6)
C(16)	−1 220(3)	1 634(3)	3 246(2)	308(3)	−285(2)	3 248(6)
C(17)	−2 153(4)	2 388(3)	3 281(3)	−728(4)	−169(3)	2 201(7)
C(18)	−1 919(4)	2 938(3)	4 036(3)	−995(4)	343(3)	1 081(7)
C(19)	−773(4)	2 716(3)	4 729(3)	−251(4)	738(3)	1 027(7)
C(20)	108(2)	1 953(3)	4 659(2)	766(4)	606(2)	2 111(7)
N(4)	−104(2)	1 411(2)	3 936(2)	1 042(3)	108(2)	3 213(5)
Cl(2)	3 602(1)	1 061(1)	1 338(1)			
O(1)	4 122(3)	548(4)	784(2)			
O(2)	3 232(5)	262(3)	1 794(3)			
O(3)	2 519(3)	1 730(3)	891(2)			
O(4)	4 629(3)	1 687(3)	1 957(2)			
N(5)				4 038(5)	2 524(3)	8 368(11)
O(1)				3 295(6)	2 268(3)	7 319(9)
O(2)				4 337(7)	2 361(4)	9 961(9)
O(3)				4 480(5)	2 930(4)	8 035(10)
O(4)				1 535(5)	1 934(3)	706(7)
O(5)				2 483(4)	1 392(3)	8 638(8)
O(6)				1 533(4)	2 423(3)	3 840(8)

trigonal-bipyramidal stereochemistry. The Cu–N(1) and Cu–N(3) distances in (1) and (2) are not significantly different (average 1.99 Å) and the N(1)–Cu–N(3) angles (α_8, Figure 1) are close to 180° (average 174.7°). The average in-plane Cu–N distances of 2.106 and 2.101 Å for (1) and (2), respectively, are not significantly different, but are *ca.* 0.1 Å larger than the average Cu–N out-of-plane distances, Cu–N(1) and Cu–N(3), and are as previously observed for trigonal-bipyramidal copper(II) complexes.[27] In (1) and (2) the Cu–N(4) distances are significantly greater than the Cu–N(2) distances and ΔN [Cu–N(4) − Cu–N(2)] equals 0.06 and 0.023 Å, respectively. The Cu–Cl distances in (1) and (2) are also significantly different, at 2.263 and 2.308 Å, respectively.

TABLE 3

Selected bond lengths (Å) with estimated standard deviations in parentheses

	(1) $[Cu(bipy)_2Cl][ClO_4]$	(2) $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$
Cu–Cl(1)	2.263(3)	2.308(3)
Cu–N(1)	1.993(4)	1.989(6)
Cu–N(2)	2.076(3)	2.089(6)
Cu–N(3)	1.991(4)	1.989(6)
Cu–N(4)	2.136(5)	2.112(5)
O(1)–Cl(2)	1.412(5)	
O(2)–Cl(2)	1.396(6)	
O(3)–Cl(2)	1.393(5)	
O(4)–Cl(2)	1.428(4)	
O(1)–N(5)		1.182(10)
O(2)–N(5)		1.245(12)
O(3)–N(5)		1.168(13)

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

	(1) $[Cu(bipy)_2Cl][ClO_4]$	(2) $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$
N(1)–Cu–Cl(1)	93.4(2)	93.1(2)
N(2)–Cu–Cl(1)	137.1(1)	127.8(2)
N(2)–Cu–N(1)	80.1(2)	79.9(3)
N(3)–Cu–Cl(1)	92.1(2)	92.0(2)
N(3)–Cu–N(1)	174.5(1)	174.9(2)
N(4)–Cu–N(2)	96.0(2)	96.6(2)
N(4)–Cu–Cl(1)	126.4(2)	123.4(2)
N(4)–Cu–N(1)	97.4(2)	97.6(2)
N(4)–Cu–N(2)	96.5	108.8(2)
N(4)–Cu–N(3)	79.2(2)	80.0(2)
O(2)–Cl(2)–O(1)	109.0(4)	
O(3)–Cl(2)–O(1)	111.0(3)	
O(3)–Cl(2)–O(2)	111.2(4)	
O(4)–Cl(2)–O(1)	109.8(3)	
O(4)–Cl(2)–O(2)	105.8(3)	
O(4)–Cl(2)–O(3)	109.9(3)	
O(2)–N(5)–O(1)		116.6(10)
O(3)–N(5)–O(1)		125.2(9)
O(3)–N(5)–O(2)		118.2(8)

In both (1) and (2) the out-of-plane angular distortions are comparable (Table 4) and near 90 ± 10°, but there are significant differences in the in-plane angles, α_{1-3},

which not only differ from the 120° of a regular trigonal-bipyramidal stereochemistry, but are different in (1) and (2); α_1 and α_2 are greater than 120° (Table 4) and α_3 is less than 120°, α_1 is greater in (1) than in (2) (137.1 and 127.8° respectively), and α_3 is lower in (1) than in (2) (96.5° and 108.8° respectively) and suggests that the in-plane angular distortions, from 120°, are greater in (1) than in (2). In both complexes the large α_1 angles are opposite the longest Cu–N(4) distance.

The structure of the $[Cu(bipy)_2Cl]^+$ cation has been previously reported in three complexes: $[Cu(bipy)_2Cl]_2[S_5O_6]\cdot 6H_2O$ [13] (3), $[Cu(bipy)_2Cl][CuCl_2]$ [14] (4), and $[Cu(bipy)_2Cl]Cl\cdot 6H_2O$ [17] (5). Consequently, the five complexes (1)—(5) represent a series of cation distortion isomers of the $[Cu(bipy)_2Cl]^+$ cation and offer the opportunity to examine the structure of this cation in *five* different crystal environments. Table 6 summarises the structural data for (1)—(5) using the notation of Figure 1. While all five complexes contain the [Cu(bipy)$_2$Cl] structural unit, only in (1), (2), (3), and (5) is this present as a distinct cation; in (4) the chloride ion is involved in a bridging role [14] to the copper(I) of the $[CuCl_2]^-$ anion. All five complexes contain a distorted trigonal-bipyramidal CuN_4Cl chromophore, but while the structure in (5) involves as near a regular trigonal-bipyramidal CuN_4Cl chromophore as a system with non-equivalent ligands can have, that of (1) has a clearly distorted structure (distorted towards a square-pyramidal structure with N(1), N(2), N(3), and Cl atoms constituting the basal plane about the copper atom and the N(4) atom occupying the fifth ligand position). The structures of (2) and (3) involve intermediate distortions, with (2) more distorted than (3).

TABLE 5

Summary of some relevant mean planes

	(1) $[Cu(bipy)_2Cl][ClO_4]$ r.m.s.d.*	(2) $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$ r.m.s.d.*
Plane 1: N(1), C(1)—C(5)	0.005 8	0.005 0
Plane 2: N(2), C(6)—C(10)	0.004 3	0.005 4
Plane 3: N(1), N(2), C(1)—C(10)	0.092 0	0.013 8
Plane 4: N(3), C(11)—C(15)	0.000 2	0.007 1
Plane 5: N(4), C(16)—C(20)	0.006 2	0.007 8
Plane 6: N(3), N(4), C(11)—C(20)	0.034 0	0.012 6
Angles between planes (°)		
1 : 2	10.85	1.75
4 : 5	3.97	0.71
3 : 6	88.54	72.10

* Root mean square deviation in Å ($\times 10^3$).

In all five complexes the out-of-plane Cu–N distances are not significantly different (mean 1.99 ± 0.02 Å) and the mean in-plane Cu–N distances are consistently longer [Cu–N(2) 2.079 ± 0.02 Å and Cu–N(4) 2.104 ± 0.03 Å]. The Cu–Cl bond distances are consistently longer than the Cu–N distances, due to the larger size of the chlorine atom (mean 2.31 ± 0.05 Å). While the differences in the distances of Cu to N(1), N(2), and N(3) atoms is not significant, those for the Cu to N(4) and Cl atoms are significantly different, and suggest that in the series (1) to (5) the Cu–N(4) distance systematically decreases and the Cu–Cl distance increases. Figure 3(*a*) shows a plot of the Cu–N(4) distance against the Cu–Cl distance, and Figure 3(*b*) shows the corresponding copper–ligand distances corrected for the normal covalent bond distance [28] (2.00 Å for Cu–N and 2.30 Å for Cu–Cl).

TABLE 6

Some relevant bond lengths (Å) and bond angles (°) for the trigonal-bipyramidal CuN_4Cl chromophore in $[Cu(bipy)_2Cl]X$ *

	(1)	(2)	(3)	(4)	(5)
Cu–N(1)	1.993(4)	1.989(6)	1.992(6)	1.985	1.989(10)
Cu–N(3)	1.991(4)	1.989(6)	1.988(6)	1.995	1.970(10)
Cu–N(2)	2.076(3)	2.089(6)	2.092(6)	2.063	2.077(10)
Cu–N(4)	2.136(5)	2.112(5)	2.106(5)	2.086	2.087(11)
Cu–Cl	2.263(3)	2.308(3)	2.292(4)	2.356	2.361(4)
α_1[N(2)–Cu–Cl]	137.1	127.8	130.7	133.4	118.7
α_2[N(4)–Cu–Cl]	126.4	123.4	122.0	111.1	118.6
α_3[N(2)–Cu–N(4)]	96.5	108.8	107.3	115.5	122.8
α_4[N(1)–Cu–Cl]	93.4	93.1	92.0	91.0	90.9
α_5[N(3)–Cu–Cl]	92.1	92.0	93.3	93.5	90.9
α_6[N(1)–Cu–N(2)]	80.1	79.9	79.9	80.0	79.3
α_7[N(3)–Cu–N(4)]	79.2	80.0	79.7	80.2	79.8
α_8[N(1)–Cu–N(3)]	174.5	174.9	174.8	175.3	178.3
α_9[N(1)–Cu–N(4)]	97.4	97.6	97.5	97.8	99.3
α_{10}[N(3)–Cu–N(2)]	96.0	96.6	96.7	97.0	100.0
α_{11}[Twist N(1)/N(2)]	3.97	0.63	2.31	3.16	0.0
α_{12}[Twist N(3)/N(4)]	10.85	1.25	2.31	7.01	0.0

* X = ClO_4 (1), $[NO_3]\cdot 3H_2O$ (2), $\frac{1}{2}\{[S_5O_6]\cdot 6H_2O\}$ (3), Cu^ICl_2 (4), and $Cl\cdot 6H_2O$ (5).

All the out-of-plane angles α_4—α_{10} (Table 6) are com-

parable and show no systematic variation in the series (1) to (5); an exception could be α_8, which is much closer to 180° (178.3°) in (5) than in the remaining complexes (mean 174.9°). All three in-plane angles, α_1—α_3, show appears to be anomalous, possibly due to the bridging role [14] of the Cl atom involved (see above). The in-plane angles are most distorted from 120° in (1) and least distorted in (5), which has a near regular trigonal-

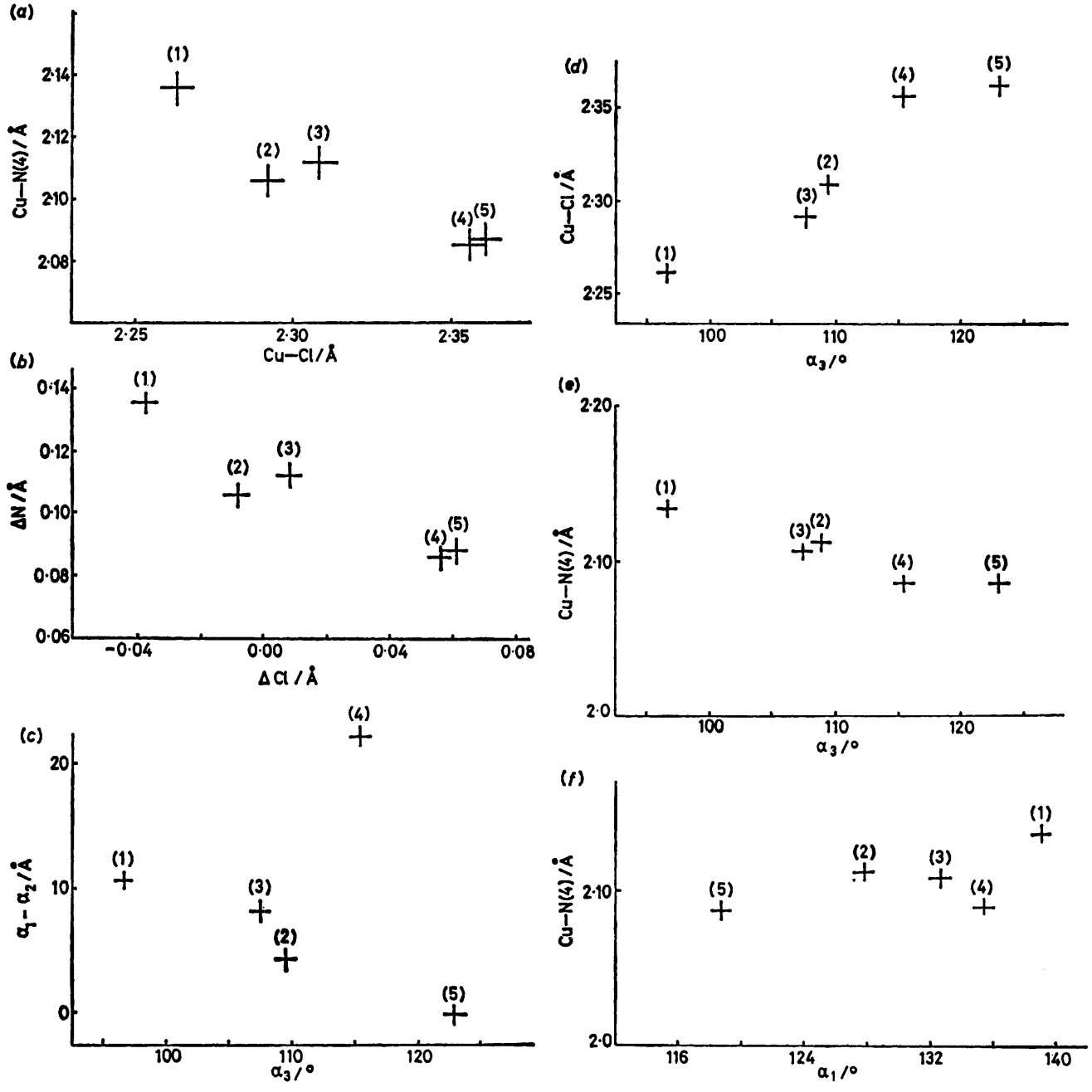


FIGURE 3 Plots for the complexes (1)—(5) of (*a*) Cu–Cl *vs.* Cu–N(4) distances; (*b*) ΔCl *vs.* ΔN (see text for definition); (*c*) α_3 *vs.* $\alpha_1 - \alpha_2$; (*d*) α_3 *vs.* Cu–Cl; (*e*) α_3 *vs.* Cu–N(4); (*f*) α_1 *vs.* Cu–N(4)

significant deviation from the 120° predicted for a regular trigonal-bipyramidal structure; the α_1 angles are significantly greater than 120° and decrease (1) to (5), the α_3 angles are significantly less than 120° and increase (1) to (5), and α_2 is greater than 120° in (1)—(3), but less than 120° in (4) and (5). The α_2 angle of 111.1° in (4) bipyramidal stereochemistry. Figure 3(*c*) shows a plot of $\alpha_1 - \alpha_2$ against α_3, Figure 3(*d*) that of the Cu–Cl distance against α_3, Figure 3(*e*) that for the Cu–N(4) distance against α_3, and Figure 3(*f*) that for the Cu–N(4) distance against α_1. With the exception of the angular data for (4) (see above) all four Figures suggest significant

correlation between the bond-angle distortions present and between the bond distances and the bond angles.

Thus the data of Table 6 and Figure 3 suggest for the series of complexes (1) to (5) that the observed difpyramidal distortion with elongation along the Cu–N(4) direction in (1) and is reminiscent of one of the pathways associated with the mechanistic pathway of the ' Berry Twist '.[29] The latter involves the conversion of a regular

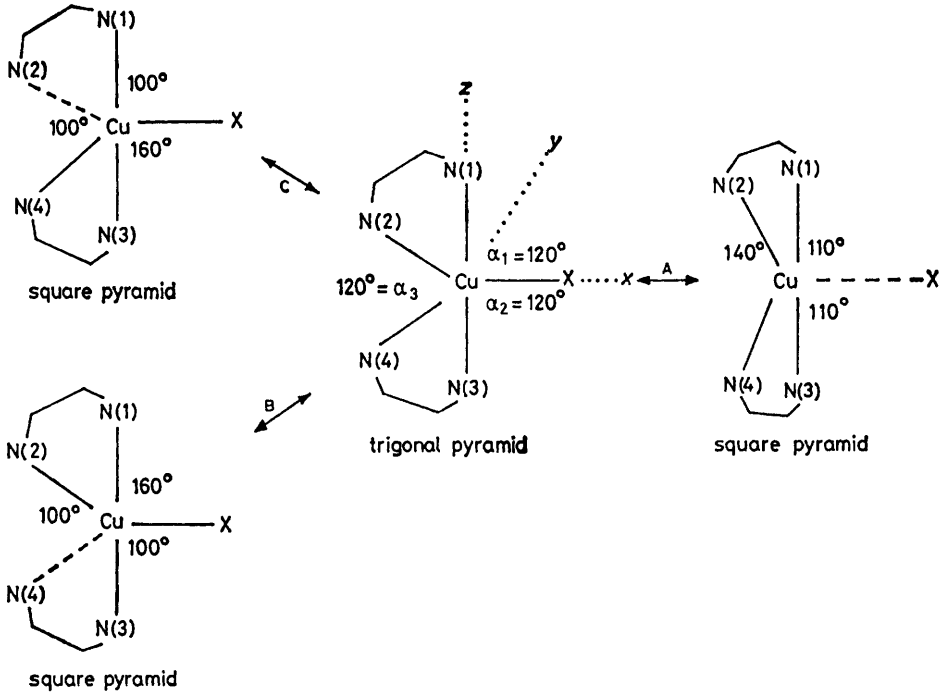


FIGURE 4 The structural pathways for the distortion of the CuN_4Cl chromophore of the $[Cu(bipy)_2Cl]X$ complexes, from trigonal-bipyramidal to square-pyramidal involving three alternative routes (A, B, and C)

ferences in some of the bond distances and bond angles in the $[Cu(bipy)_2Cl]^+$ cations are not random, but establish a systematic variation in the structure of this cation in the sequence. The sense of this systematic distortion of the CuN_4Cl chromophore is from an almost regular trigonal-bipyramidal structure in (5) towards a square-

trigonal-bipyramidal structure to a regular square-pyramidal structure related by a mode of vibration and retaining a C_2 axis of symmetry. The trigonal-bipyramidal CuN_4Cl chromophore of the cation may also be distorted towards a square-pyramidal structure by the three possible distortion routes A, B, and C of Figure 4,

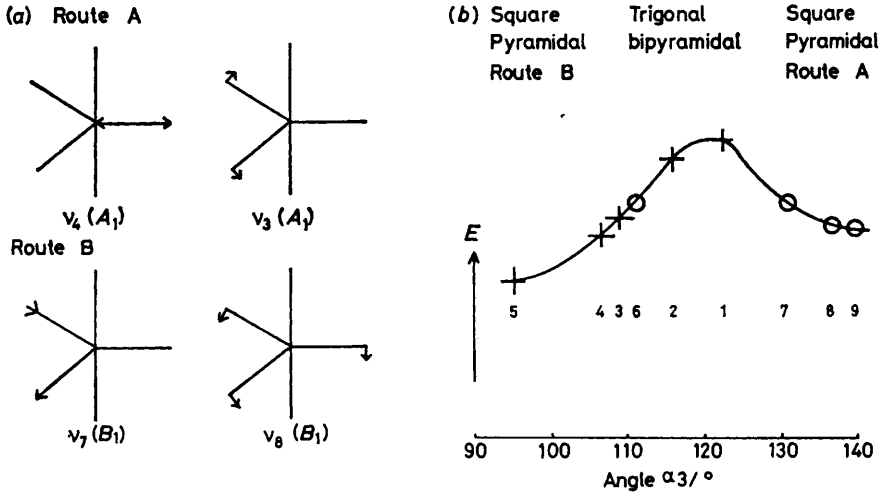
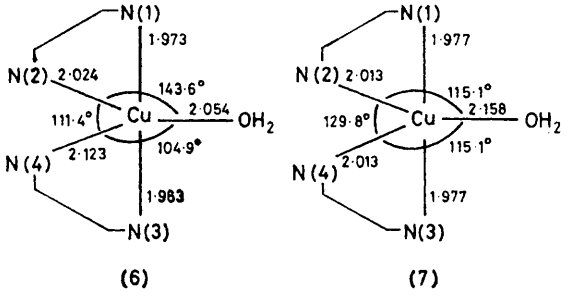


FIGURE 5 (*a*) The forms of the normal modes of vibration of a trigonal-bipyramidal $CuN_2N'_2Cl$ chromophore of C_2 symmetry (routes A and B, Figure 4). (*b*) The structural profile for complexes (1)—(9) of the $[Cu(bipy)_2Cl]^+$ cation, showing the total energy, E, against α_3 (+ = $[Cu(bipy)_2Cl]^+$, ○ = $[Cu(bipy)_2(OH_2)]^{2+}$)

which arise from the lower symmetry of the CuN_4Cl unit (approximately C_2), but due to the equivalence of the two bipy ligands, routes B and C are the same. Only the route A distortion retains a C_2 axis of symmetry and can be considered as a Berry Twist-type mechanistic pathway. In route B or C the C_2 axis of symmetry is removed and the Berry Twist analogy is lost. For this reason, it may be better to consider the three distortion pathways of Figure 4 as being related by a linear combination of the normal modes of vibration of a CuN_4Cl chromophore of C_{2v} symmetry,[30] namely, $\nu_4(A_1)$, $\nu_3(A_1)$, $\nu_7(B_1)$, and $\nu_8(B_1)$, Figure 5(*a*). The route A distortion is determined by a linear combination of the $\nu_4 + \nu_3$ (A_1 symmetry) modes of vibration and the B (or C) routes by a linear combination of $\nu_7 + \nu_8$ (B_1 symmetry) modes of vibration. The A and B (or C) routes of distortion (Figure 4) may then be represented by the structural profile [10-12] of Figure 5(*b*), where *E* represents the potential energy of the structures along the structural pathway



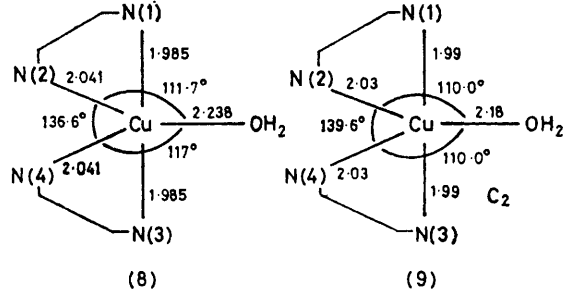


FIGURE 6 The local molecular stereochemistries of the $CuN_4(OH_2)$ chromophores in $[Cu(bipy)_2(OH_2)][S_5O_6]$, (6), $[Cu(bipy)_2(OH_2)][S_2O_6]$, (7), $[Cu(phen)_2(OH_2)][BF_4]_2$, (8), and $[Cu(phen)_2(OH_2)][NO_3]_2$, (9)

as a function of a structural parameter, such as the α_3 angle and the Cu–Cl or Cu–N(4) bond distances. As all five complexes (1)—(5) exist at room temperature, they must have comparable thermodynamic stability; nevertheless, the choice of the trigonal-bipyramidal structure with a slightly higher energy is justified as this near regular structure is less common in $[Cu(bipy)_2Cl]X$ complexes than the distorted square-pyramidal structure.

To-date there is no structural evidence for the route A mode of distortion of the $[Cu(bipy)_2Cl]^+$ cation, but both the A and B routes are represented in the cation distortion isomers of the $[Cu(bipy)_2(OH_2)]^{2+}$ cation in $[Cu(bipy)_2(OH_2)][S_5O_6]$ [13] (6), and $[Cu(bipy)_2(OH_2)][S_2O_6]$ [31] (7), and of the $[Cu(phen)_2(OH_2)]^{2+}$ cation in the A route in $[Cu(phen)_2(OH_2)][BF_4]_2$ [32] (8), and $[Cu(phen)_2(OH_2)][NO_3]_2$ [33] (9), Figure 6. Each of the various structures of Table 6 and Figure 6 then represent individual points along the two alternative pathways of the structural profile, Figure 5(*b*), and the precise geometry of each structure is determined by a number of relatively weak crystal packing forces, such as hydrogen bonding and van der Waals forces. Forces which are weak by normal standards, but due to the plasticity of the copper(II) ion,[5] are able to bring about crystallographically significant bond-length and bond-angle distortions of the CuN_4Cl or CuN_4O chromophores consistent with the structures along the routes of the structural profile. It may be significant that the extreme distortions of the routes A and B (or C) involve the copper(II) ion in its preferred prolate ellipsoidal shape [1,2] (due to its d^9 configuration) rather than the oblate ellipsoidal shape of the symmetrical trigonal-bipyramidal stereochemistry and involves a significant switch of the principal axes by 90°. Equally, it is not possible to pinpoint the particular lattice factors which generate a precise distortion; the lattice of (5), with six water molecules of hydration, contains [17] a much more extensive hydrogen-bonded network, producing a rather softer lattice in which the chloride ions are extensively disordered. The lattice of (1) is anhydrous and devoid of any short hydrogen-bond contacts; contacts greater than 3.1 Å (Table 7) do occur,

TABLE 7

Selected short bond contacts in $[Cu(bipy)_2Cl][ClO_4]$, (1), and $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$, (2)

(1) $[Cu(bipy)_2Cl][ClO_4]$	
C(3) . . . O(1)(i)	3.403
C(8) . . . O(1)(iv)	3.358
C(8) . . . O(4)(iv)	3.345
C(9) . . . O(3)(iv)	3.316
C(9) . . . O(4)(iv)	3.209
C(10) . . . O(3)(iv)	3.366
C(13) . . . O(1)(iv)	3.174
C(14) . . . O(4)(iv)	3.369
C(18) . . . O(2)(i)	3.255
C(19) . . . O(3)(i)	3.409
C(20) . . . O(3)(i)	3.100
(i) x, y, z (iv) $x, 0.5 - y, 0.5 + z$	
(2) $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$	
Cl . . . O(5)(i)	3.216
C(1)–H(1) . . . O(1)(i)	3.396
C(10)–H(8) . . . O(1)(iii)	3.342
C(11)–H(9) . . . O(6)(iii)	3.377
C(13)–H(11) . . . O(6)(iii)	3.299
C(20)–H(16) . . . O(4)(i)	3.399
O(4)–H(18) . . . O(3)(i)	2.849
(i) x, y, z (iii) $0.5 + x, 0.5 - y, -z$	

but do not involve hydrogen atoms. These contacts are between oxygen atoms of the ClO_4^- ions and the carbon atoms of the bipy ligands, with the planes of the latter approximately parallel to a three-oxygen-atom plane of the ClO_4 tetrahedra, Figure 7(*a*) and (*b*). These contacts might be responsible for the lowest value of α_3 in (1), but they cannot explain the relatively low value of α_3 in (2),

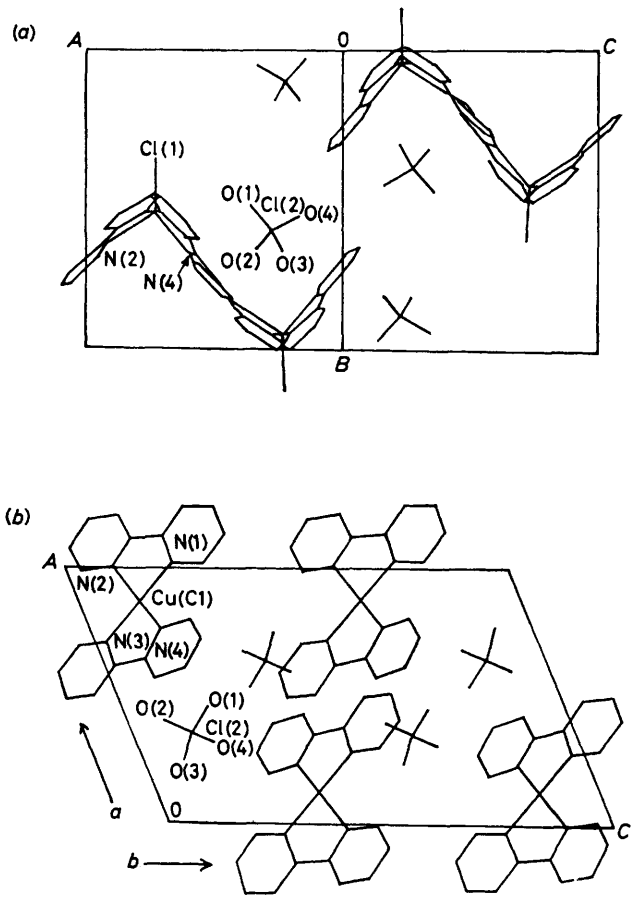


FIGURE 7 The projection of $[Cu(bipy)_2Cl][ClO_4]$ (*a*) down the bisector of the *a* and *c* axes and (*b*) the projection down the *b* axis

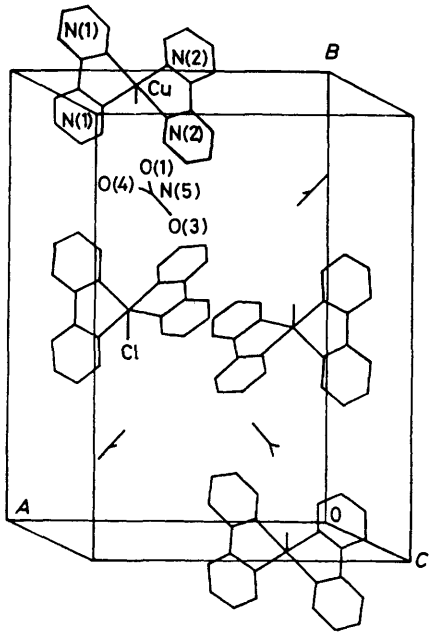


FIGURE 8 A projection of the unit cell of $[Cu(bipy)_2Cl][NO_3]\cdot 3H_2O$ down the Cu-Cl direction of the CuN_4Cl chromophores

where there is no such correlation of the plane of the nitrate ion with the planes of the ligands (Figure 8). In (2) there are a number of moderately short contacts some involving hydrogen bonds, to both the nitrate oxygen O(1)–O(3) and to the lattice water molecules. One of these, the O(4)–H(18) · · · O(3) contact, represents a moderately strong bond (2.849 Å) and suggests that the O(4) water molecule is strongly associated with the nitrate ion.

The structural profile of Figure 5(*b*) may also be used to rationalise the distorted stereochemistries of a wider range of $[Cu(chelate)_2L]X_2$ (X = halide) complexes,[16,34] where L may vary as ammonia,[35] cyanide,[36] thiocyanate,[36] nitrite,[37] acetate,[38] and formate,[39] using plots of the $(\alpha_1 - \alpha_2)$ angles against the α_3 angles (see Figure 6 of ref. 34).

Electronic Criteria of Stereochemistry.—All five complexes (1)—(5) are green-blue and their electronic reflectance spectra are shown in Figure 2. The spectrum of (5), the most regular trigonal-bipyramidal structure, has a single broad absorption at 12 500 cm^{-1} while there is a significant splitting in the complexes (3), (2), and (1), with a maximum splitting of 4 060 cm^{-1} in (1), the complex with the greatest distortion towards square-pyramidal. This suggests that the more regular trigonal CuN_4Cl chromophores will have a single broad peak in their electronic spectra and the distorted square-pyramidal chromophores will have a clear splitting, *ca.* 4 000 cm^{-1}, a difference first noted [31] for the two cation distortion isomers (6) and (7), where (6) has a clear splitting (10 750 and 14 120 cm^{-1}) while (7) has a single peak at 12 450 cm^{-1}. Together, this suggests that there may be a spectroscopic criteria of stereochemistry [40] to distinguish these different structures, especially the regular trigonal-bipyramidal CuN_4Cl chromophore from the B (or C) route of square-pyramidal distortion.

We acknowledge the award of a Department of Education Postdoctoral Fellowship (to R. S.), help in data collection by Drs. P. G. Owston, M. McPartlin, and K. Henrick (Polytechnic of North London, Holloway), the Computer Bureau, U.C.C. for computing facilities, Drs. G. Sheldrick, S. Motherwell, and R. Taylor (Cambridge University) for the use of their programs, and the Microanalysis Section, U.C.C. for microanalysis.

[0/1776 *Received*, 18*th November*, 1980]

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