Crystal Structure and Electronic Properties of Bis(2,2′-bipyridyl)formatocopper(II) Tetrafluoroborate–Water (2/1)

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The crystal structure of the title compound, (1), has been determined by *X*-ray analysis. Compound (1) crystallises in the triclinic space group $P\bar{1}$ with a = 7.570(2), b = 9.742(2), c = 14.994(2) Å, α = 100.376(4), β = 96.806(3), γ = 86.107(3)°, and Z = 2. The six-co-ordinate CuN_4OO' chromophore has a (4 + 1 + 1*) stereochemistry related to the regular *cis*-distorted octahedral stereochemistry by an in-plane twist towards a square-pyramidal CuN_4O stereochemistry by the mechanistic pathway of the Berry twist. The single-crystal e.s.r. spectra of (1) and acetatobis(2,2′-bipyridyl)copper(II) perchlorate monohydrate, (2), are clearly rhombic and correlate with the square-pyramidal rather than the *cis*-distorted octahedral stereochemistry of the CuN_4OO' chromophore, when large Cu–O(2) distances are involved.

IN [Cu(bipy)$_2$X]Y (bipy = 2,2′-bipyridyl) complexes the local molecular structures of the CuN_4L [1,2] and CuN_4(OXO) [3,4] chromophores (where L is a unidentate ligand and OXO^- is a bidentate chelate ligand), Figure 1, involve a regular trigonal bipyramidal [5] and a *cis*-distorted octahedral stereochemistry,[3,6,7] respectively. But there is increasing crystallographic evidence [2,8] that the former may undergo appreciable distortion along the alternative mechanistic pathways of the Berry twist [9,10] (A) and (B) of Figure 1(*a*), with elongation along the Cu–L and Cu–N(4) directions respectively. If the OXO^- anion is considered [11] to involve a single co-ordinate site, when co-ordinated symmetrically, Figure 1(*b*), then the *cis*-distorted octahedral stereochemistry can also undergo the two corresponding alternative distortion routes (C) and (D), Figure 1(*b*). When OXO^- is the nitrite,[3,12] acetate,[4,6,7] or formate [13] ion the observed distortion lies along route (D), towards square pyramidal, a sense of distortion that implies a rotation of the x and y axes to the alternative positions X^1 and Y^1, Figure 2, with a corresponding rotation of the g_x and g_y local molecular directions. To date, it has not been possible to determine experimentally this change in direction of the local molecular g factors, with respect to the copper–nitrogen and –oxygen directions. Since this information is best obtained from triclinic crystals, space group $P\bar{1}$, and since [Cu(bipy)$_2$(O$_2$CH)][BF$_4$]·0.5H$_2$O, (1), has this space group, the crystal structure of (1) has been determined and the single-crystal e.s.r. spectra of (1) and [Cu(bipy)$_2$(O$_2$CMe)][ClO$_4$]·H$_2$O†, (2), which also crystallises [4] in the triclinic space group $P\bar{1}$, have been determined and are now reported.

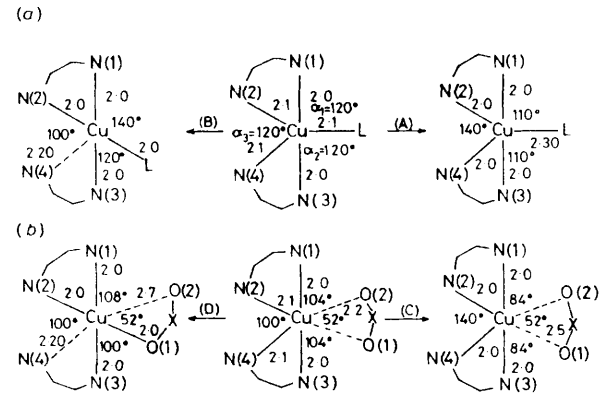

FIGURE 1 The alternative routes for distortion towards square pyramidal of (*a*) a trigonal bipyramidal [Cu(bipy)$_2$L]Y system and (*b*) a *cis*-distorted octahedral [Cu(bipy)$_2$(OXO)]Y system

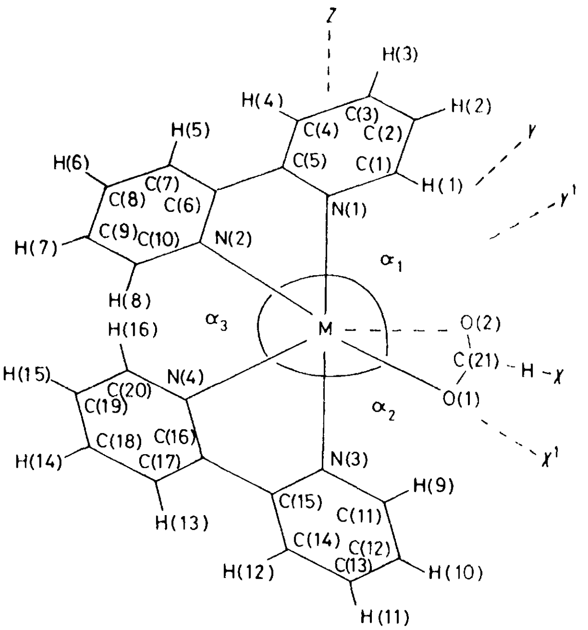

FIGURE 2 The molecular structure of the [Cu(bipy)$_2$(O$_2$CH)]$^+$ cation and atom-numbering scheme used

EXPERIMENTAL

Preparation.—Complex (1) was prepared by adding bipy (1 g, 6.4 mmol) in a water–acetone (20 cm^3, 1 : 1) mixture to [Cu(OH$_2$)][$_6$BF$_4$]$_2$ (1.11 g, 3.2 mmol) in a water–acetone (80 cm^3, 1 : 1) mixture, the solution was then boiled, and a drop of technical aqueous HBF$_4$ solution was added plus Na[O$_2$CH] (0.653 g, 9.6 mmol, a three-fold excess) dissolved

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† The stereochemistry of the CuN_4OO' chromophore of (2) is comparable to (1), Figure 2, with Cu to N(1) = 1.971, N(2) = 2.056, N(3) = 1.994, N(4) = 2.168 Å, Cu to O(1) = 2.031, O(2) = 2.648 Å, α_1 147.6, α_2 = 100.7, α_3 = 111.6°.

in water (10 cm^3). The resulting blue solution was boiled, filtered, and allowed to stand at room temperature. After 2—3 days, dark royal blue crystals were deposited (Found: C, 50.3; H, 4.05; Cu, 12.8; N, 11.2. $C_{21}H_{18}BCuF_4N_4O_{2.5}$ requires C, 48.8; H, 3.50; Cu, 12.3; N, 10.85%). Complex (2) was prepared as previously reported.[4]

Crystal Data.—$C_{21}H_{18}BCuF_4N_4O_{2.5}$, $M = 525.35$, Triclinic, $a = 7.570(2)$, $b = 9.742(2)$, $c = 14.994(2)$ Å, $\alpha = 100.376(4)$, $\beta = 96.806(3)$, $\gamma = 86.107(3)°$, $U = 1\,078.79$ Å^3, D_m (flotation) $= 1.611 \pm 0.02$ g cm^{-3}, $Z = 2$, $D_c = 1.617$ g cm^{-3}, $F(000) = 513.98$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 10.28, space group $P\bar{1}$, no systematic absences.

Preliminary unit-cell dimensions and space-group data were obtained from precession photographs and refined on a Philips PW 1100 four-circle diffractometer. The intensities were collected on the diffractometer with graphite-monochromatised Mo-K_α radiation. A θ—2θ scan mode was used and reflections with $3.0 < \theta < 32°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} was used with a variable scan width of $(0.7 + 0.1 \tan\theta)°$. With an acceptance criterion of $I > 2.5\sigma(I)$, 3 199 reflections were retained. Lorentz and polarisation corrections were applied, but no correction was made for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked-matrix least squares with anisotropic temperature factors for all of the non-hydrogen atoms except the water molecules. The positions of the hydrogen atoms were calculated geometrically (except for the disordered water molecule) and floated on the associated carbon or oxygen atoms, assuming C–H or O–H = 1.08 Å and a fixed temperature factor of 0.07 Å^2. The refinement converged when the shift-to-error ratio of any parameter was less than 0.04, with a refined weighting scheme, $w = k/[\sigma^2(F_o) + g(F_o)^2]$ and the final values of k and g were 1.510 7 and 0.000 144 respectively. Complex atomic scattering factors[14] were employed and the Cu atom was corrected for anomalous dispersion. The final R values were $R = 0.044\,3$ and $R' = 0.048\,6$ with a maximum residual electron density of 0.51 e Å^{-3}. All calculations were carried out with SHELX-76[15] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and XPUB (R. Taylor) on an IBM 370/138 computer. The final atomic co-ordinates are given in Table 1, the bond lengths in Table 2, the bond angles in Table 3; Table 4 gives some relevant mean planes. The final structure factors, anisotropic temperature factors, and the calculated hydrogen-atom positions are given in Supplementary Publication No. SUP 22944 (23 pp.).*

TABLE 1

Atom co-ordinates (× 10^4) of $[Cu(bipy)_2(O_2CH)][BF_4]\cdot 0.5H_2O$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu	4 384(1)	197(1)	2 430(1)
N(1)	4 387(4)	−1 215(3)	3 227(2)
C(1)	5 161(6)	−2 513(4)	3 043(3)
C(2)	4 991(6)	−3 497(4)	3 585(3)
C(3)	4 061(6)	−3 131(4)	4 329(3)
C(4)	3 301(5)	−1 796(4)	4 534(3)
C(5)	3 479(5)	−855(4)	3 957(2)
C(6)	2 719(4)	600(4)	4 094(2)
C(7)	1 892(5)	1 204(4)	4 850(3)
C(8)	1 240(6)	2 564(5)	4 919(3)
C(9)	1 407(6)	3 279(5)	4 220(3)
C(10)	2 225(6)	2 613(4)	3 475(3)
N(2)	2 902(4)	1 298(3)	3 415(2)
N(3)	4 203(4)	1 581(3)	1 582(2)
C(11)	4 931(5)	2 836(4)	1 793(3)
C(12)	4 820(5)	3 758(4)	1 200(3)
C(13)	3 967(5)	3 359(4)	332(3)
C(14)	3 271(5)	2 044(4)	83(3)
C(15)	3 404(4)	1 177(3)	733(2)
C(16)	2 685(4)	−236(3)	543(2)
C(17)	1 950(5)	−852(4)	−324(2)
C(18)	1 286(5)	−2 170(4)	−434(3)
C(19)	1 338(5)	−2 836(4)	306(3)
C(20)	2 108(5)	−2 156(4)	1 152(3)
N(4)	2 774(4)	−886(3)	1 265(2)
O(1)	6 854(4)	−431(3)	2 087(2)
C(21)	8 032(6)	−24(5)	2 693(3)
O(2)	7 823(6)	739(4)	3 415(2)
O(3)	2 809(8)	6 441(6)	6 169(4)
B	−485(7)	5 564(5)	2 267(3)
F(1)	−1 619(4)	5 978(4)	1 585(2)
F(2)	967(5)	4 881(4)	1 917(3)
F(3)	−1 355(5)	4 678(5)	2 648(3)
F(4)	27(5)	6 695(4)	2 874(3)

TABLE 2

Bond lengths (Å) for $[Cu(bipy)_2(O_2CH)][BF_4]\cdot 0.5H_2O$ with estimated standard deviations in parentheses

N(1)–Cu	1.978(5)	N(2)–Cu	2.061(5)
N(3)–Cu	2.001(5)	N(4)–Cu	2.158(5)
O(1)–Cu	2.024(5)	O(2)–Cu	2.869(12)
C(5)–N(1)	1.343(6)	C(1)–N(1)	1.353(6)
C(3)–C(2)	1.370(8)	C(2)–C(1)	1.384(7)
C(5)–C(4)	1.392(7)	C(4)–C(3)	1.383(7)
C(7)–C(6)	1.379(6)	C(6)–C(5)	1.481(6)
C(8)–C(7)	1.372(7)	N(2)–C(6)	1.347(6)
C(10)–C(9)	1.378(7)	C(9)–C(8)	1.381(8)
C(11)–N(3)	1.345(6)	N(2)–C(10)	1.339(6)
C(12)–C(11)	1.366(7)	C(15)–N(3)	1.346(5)
C(14)–C(13)	1.390(6)	C(13)–C(12)	1.384(6)
C(16)–C(15)	1.482(6)	C(15)–C(14)	1.391(6)
N(4)–C(16)	1.343(6)	C(17)–C(16)	1.396(5)
C(19)–C(18)	1.378(8)	C(18)–C(17)	1.386(7)
N(4)–C(20)	1.343(6)	C(20)–C(19)	1.400(6)
O(2)–C(21)	1.218(6)	C(21)–O(1)	1.226(6)
F(2)–B	1.355(7)	F(1)–B	1.356(7)
F(4)–B	1.344(7)	F(3)–B	1.359(8)

TABLE 3

Bond angles (°) for $[Cu(bipy)_2(O_2CH)][BF_4]\cdot 0.5H_2O$ with estimated standard deviations in parentheses

N(2)–Cu–N(1)	80.3(2)	N(3)–Cu–N(1)	175.8(1)
N(3)–Cu–N(2)	99.1(2)	N(4)–Cu–N(1)	97.5(2)
N(4)–Cu–N(2)	113.2(2)	N(4)–Cu–N(3)	78.9(2)
O(1)–Cu–N(1)	92.9(2)	O(1)–Cu–N(2)	146.1(1)
O(1)–Cu–N(3)	89.9(2)	O(1)–Cu–N(4)	100.5(2)
C(1)–N(1)–Cu	123.6(4)	C(5)–N(1)–Cu	116.4(3)
C(5)–N(1)–C(1)	119.9(4)	C(2)–C(1)–N(1)	121.0(5)
C(3)–C(2)–C(1)	119.1(5)	C(4)–C(3)–C(2)	120.3(5)
C(5)–C(4)–C(3)	118.3(5)	C(4)–C(5)–N(1)	121.3(4)
C(6)–C(5)–N(1)	114.9(4)	C(6)–C(5)–C(4)	123.8(4)
C(7)–C(6)–C(5)	123.4(4)	N(2)–C(6)–C(5)	114.4(4)
N(2)–C(6)–C(7)	122.2(4)	C(8)–C(7)–C(6)	119.1(5)
C(9)–C(8)–C(7)	118.9(5)	C(10)–C(9)–C(8)	119.3(5)
N(2)–C(10)–C(9)	122.1(5)	C(6)–N(2)–Cu	113.7(3)
C(10)–N(2)–Cu	127.8(4)	C(10)–N(2)–C(6)	118.3(4)
C(11)–N(3)–Cu	123.8(3)	C(15)–N(3)–Cu	117.1(3)
C(15)–N(3)–C(11)	118.9(4)	C(12)–C(11)–N(3)	123.1(4)
C(13)–C(12)–C(11)	118.2(5)	C(14)–C(13)–C(12)	119.9(5)
C(15)–C(14)–C(13)	118.4(4)	C(14)–C(15)–N(3)	121.4(4)
C(16)–C(15)–N(3)	115.8(4)	C(16)–C(15)–C(14)	122.8(4)
C(17)–C(16)–C(15)	122.7(4)	N(4)–C(16)–C(15)	115.4(4)
N(4)–C(16)–C(17)	122.0(4)	C(18)–C(17)–C(16)	118.6(5)
C(19)–C(18)–C(17)	119.9(5)	C(20)–C(19)–C(18)	118.2(5)
N(4)–C(20)–C(19)	122.4(5)	C(16)–N(4)–Cu	111.9(3)
C(20)–N(4)–Cu	128.5(4)	C(20)–N(4)–C(16)	118.9(4)
C(21)–O(1)–Cu	112.8(4)	O(2)–C(21)–O(1)	126.2(5)
F(2)–B–F(1)	109.4(5)	F(3)–B–F(1)	107.5(5)
F(3)–B–F(2)	109.5(5)	F(4)–B–F(1)	109.1(5)
F(4)–B–F(2)	109.3(5)	F(4)–B–F(3)	112.0(5)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

Figure 2 illustrates the structure of (1) and the atom-numbering scheme used.

Electronic Properties.—These were recorded as previously described.[16,17] Figure 3(*a*) illustrates the electronic reflectance spectra of (1) and (2) and Figure 3(*b*) the polycrystalline e.s.r. spectra. The electronic spectra of both (1) and (2) involve twin peaks of comparable intensity at 10 200 and 14 360, and 9 990 and 13 880 cm^{-1} respectively.

TABLE 4

Equations of least-squares planes in the form $lx + my + nz = p$, where x, y, and z are orthogonal axes. Deviations (Å) of relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): N(1), C(1)—C(5) (root-mean-square deviation 0.0072)	6.0479	2.5814	6.2907	4.3760
[C(1) 0.0111, C(4) 0.0090]				
Plane (2): C(6)—C(10), N(2) (root-mean-square deviation 0.0069)	6.4513	2.9567	4.6177	3.8231
[C(10) −0.0102, N(2) 0.0094]				
Plane (3): N(1), C(1)—C(10), N(2) (root-mean-square deviation 0.0587)	6.2558	2.7919	5.4635	4.1044
[C(1) 0.0854, C(10) −0.0841, C(8) 0.0745]				
Plane (4): N(3), C(11)—C(15) (root-mean-square deviation 0.0120)	6.7143	−2.7517	−5.2145	1.5784
[C(11) 0.0170, N(3) −0.0163]				
Plane (5): C(16)—C(20), N(4) (root-mean-square deviation 0.0055)	6.8011	−3.1968	−3.5459	1.7147
[C(18) 0.0077, C(19) −0.0067]				
Plane (6): N(3), C(11)—C(20), N(4) (root-mean-square deviation 0.0577)	6.7801	−2.9500	−4.3859	1.6367
[C(11) 0.0835, C(13) −0.0835, C(17) 0.0785]				
Plane (7): N(1), N(2), N(3), N(4) (root-mean-square deviation 0.5472)	7.5402	0.0933	−0.6391	2.5393
[Cu 0.6126, N(1) 0.5508, N(2) −0.5573, N(3) 0.5435, N(4) −0.5370]				
Plane (8): N(1), N(2), N(3), O(1) (root-mean-square deviation 0.3217)	0.5601	4.8224	7.3667	4.1389
[Cu −0.2548, N(1) −0.3477, N(2) 0.3257, N(3) −0.2945, O(1) 0.3165]				
Plane (9): N(2), N(4), O(1)	0.8250	8.7423	−8.9314	−1.6759
Plane (10): O(1), O(2), C(21)	1.5072	8.736	−8.8041	−1.1815

Dihedral angles (°) between planes: (1)–(2) 6.87; (4)–(5) 6.72; (3)–(6) 58.32; (9)–(10) 5.29.

The e.s.r. spectra are clearly rhombic in each case, g 2.031, 2.129, and 2.208 for (1) and 2.018, 2.126, and 2.224 for (2); as both complexes (1) and (2) are triclinic, the CuN$_4$OO′ chromophores are aligned and the crystal g values are equivalent to the local molecular g factors. The single-crystal e.s.r. spectra[16] of (1) and (2) showed only *one* signal in any direction; using the six-position method,[16] the crystal g values were determined along with their directions and are reported in Table 5, along with the directions of some relevant Cu–N and Cu–O bonds.

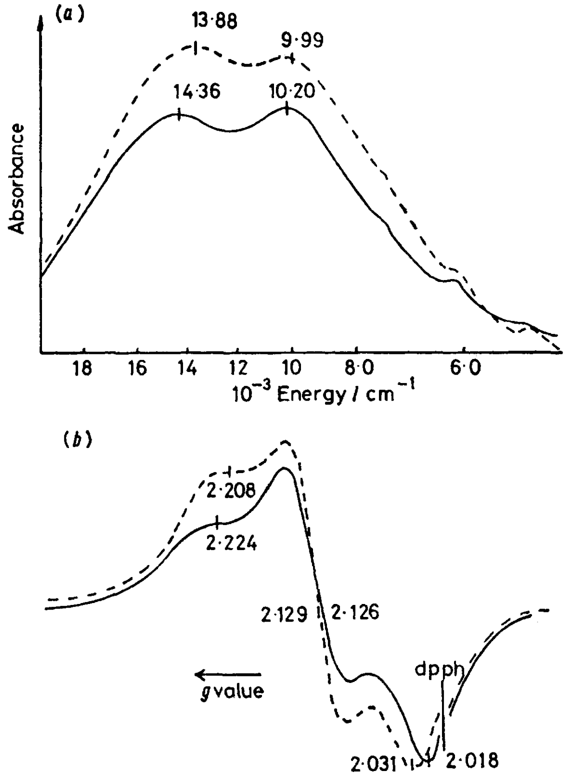

FIGURE 3 The electronic reflectance spectra (*a*) and polycrystalline e.s.r. spectra (dpph = diphenylpicrylhydrazyl) (*b*) of (1) [Cu(bipy)$_2$(O$_2$CH)][BF$_4$]·0.5H$_2$O (——) and (2) [Cu(bipy)$_2$(O$_2$CMe)][ClO$_4$]·H$_2$O (— — —)

RESULTS AND DISCUSSION

Crystal Structure.—The structure of (1) consists of a discrete [Cu(bipy)$_2$(O$_2$CH)]$^+$ cation and [BF$_4$]$^-$ anion plus a lattice water molecule with 46% occupancy of the site. There are no unusual bond lengths or bond angles in the bipy ligands[18] and the tetrafluoroborate anion involves reasonable B–F bond lengths, mean 1.351 Å, and

TABLE 5

The single-crystal g factors, their angular directions and those of some copper–ligand directions for [Cu(bipy)$_2$(O$_2$CH)][BF$_4$]·0.5H$_2$O and [Cu(bipy)$_2$(O$_2$CMe)][ClO$_4$]·H$_2$O

(*a*) [Cu(bipy)$_2$(O$_2$CH)][BF$_4$]·0.5H$_2$O [a]

	X	Y	Z
2.015	92.3	43.5	133.4
2.115 [b]	32.8	110.3	114.5
2.255	57.3	53.6	53.4
Cu–N(1)	90.0	43.0	133.0
Cu–O(1)	23.6	105.0	108.0
Cu–N(4)	56.0	59.5	49.1

(*b*) [Cu(bipy)$_2$(O$_2$CMe)][ClO$_4$]·H$_2$O [c]

	X	Y	Z
2.017	79.9	36.9	55.0
2.148 [d]	37.2	117.3	66.8
2.241	54.7	67.1	45.9
Cu–N(1)	90.0	46.0	44.0
Cu–O(1)	24.4	104.9	108.8
Cu–N(4)	62.0	73.2	34.0

[a] X Parallel to a, Y to c^*, and Z to b^*. [b] $R = 0.714$. [c] X Parallel to a, Y to b^*, and Z to c^*. [d] $R = 1.4$.

tetrahedral bond angles, mean 109.7°; nevertheless the main residual electron density (0.51 e Å^{-3}) is associated with the $[BF_4]^-$ anion and three of the fluorine atoms have high anisotropic temperature factors[4,19] (101×10^3—181×10^3 Å^2) for F(2)—F(4), but attempts to represent the anion as a disordered anion[20] failed to improve the model and are not reported. There is no evidence for semi-co-ordination[21] of the tetrafluoroborate anion or water molecule to the copper atom.

The stereochemistry of the $[Cu(bipy)_2(O_2CH)]^+$ cation of (1) is basically five-co-ordinate, but with the second oxygen of the formate group occupying the sixth co-ordination position at a distance greater than 2.4 Å, namely 2.869 Å, to give a (4 + 1 + 1*) type co-ordination, a type of co-ordination that has been previously reported for $[Cu(bipy)_2(O_2CMe)][ClO_4]{\cdot}H_2O$,[4] $[Cu(bipy)_2(O_2CMe)][BF_4]$,[4] and $[Cu(bipy)_2(ONO)][BF_4]$.[12] The CuN_4O chromophore involves a very distorted five-co-ordinate stereochemistry, intermediate between trigonal bipyramidal and square pyramidal, Figure 2, but still related to the former, Figure 1(*a*), of $[Cu(bipy)_2X]Y$ complexes, where the mean planes of the bipy ligands are inclined at *ca.* 120° to each other [in (1) this angle is 121.2°, Table 4]. This contrasts with an angle of *ca.* 45° in the distorted square-pyramidal stereochemistry of the (A) type distortion of Figure 1(*a*), as in $[Cu(bipy)_2(ONO_2)][NO_3]$[22] and $[Cu(bipy)_2(S_2O_8)]{\cdot}H_2O$.[2] In (1) the axial Cu–N(1) and Cu–N(3) distances are not significantly different, mean 1.990 Å, and the N(1)–Cu–N(3) angle is almost linear (175.8°). The mean in-plane Cu–N distance, 2.110 Å, is significantly longer than the mean out-of-plane Cu–N distance, 1.990 Å, a difference of 0.12 Å as previously reported[23] for the trigonal-bipyramidal stereochemistry; the in-plane Cu–N distances are significantly different, ΔN = 0.097 Å (see later). The in-plane O(1) distance of 2.024 Å is only slightly longer than the normal Cu–O distance[24] of *ca.* 2.00 Å, and is considerably shorter than the Cu–O(2) distance of 2.869 Å with a [Cu–O(2)] – [Cu–O(1)] distance, ΔO = 0.845 Å.

There are no unusual out-of-plane bond angles, all are 90 ± 12°, with the bites of the bipy ligands comparable at 79.6 ± 0.7°. There are significant distortions of the three in-plane angles, α_1—α_3, Figure 2, from the 120° of a regular trigonal-bipyramidal stereochemistry, Figure 1(*a*); α_1 is considerably greater than 120° at 146.1°, while α_2 and α_3 are considerably less, 100.5 and 113.2° respectively, giving rise to the type E behaviour of Figure 6, ref. 2, involving a very substantial distortion of the trigonal plane. As α_1 lies opposite the elongated Cu–N(4) bond, it could be taken as the basal angle of a square-pyramidal stereochemistry with the Cu–N(4) bond the elongated fifth ligand direction, especially in view of the near equivalence of the α_2 and α_3 angles noted above. Nevertheless, the square-pyramidal stereochemistry of (1) is not regular {as in $K[Cu(NH_3)_5][PF_6]_3$[25] which has almost equal basal angles of 166 ± 1°} but has a clear trigonal distortion of the N(1), N(2), N(3), O(1) plane [plane (8), Table 4] with the N(1)–Cu–N(3) angle 175.8° and the O(1)–Cu–N(2) angle 146.1°, which results in a large root-mean-square deviation of 0.321 7 Å, compared with a value of 0.010 5 Å in the corresponding basal plane of $K[Cu(NH_3)_5][PF_6]_3$.[25]

In (1), the Cu–N(4) elongation is restricted by the bite of the bipy ligand N(3)/N(4), of 78.9°; it has been suggested[26] that when the bipy ligand is co-ordinated to a copper(II) ion involving significant elongation of one of the Cu–N bond distances the bite angle can decrease to *ca.* 74° and the dihedral angle between the pyridine rings can increase up to 31.3°. In the N(3)/N(4) bipy ligand of (1) the bite angle of 78.9° is slightly less than that of the 80.3° of the N(1)/N(2) bipy ligand, but the dihedral angles of 6.72 and 6.87°, respectively, are not significantly different, which suggests that the N(3)/N(4) bipy ligand is not strained by the elongation of the Cu–N(4) bond.

The mean C–O distance in the asymmetrically co-ordinated formate ion of 1.222 Å is not considered to be significantly different from the value of 1.24 Å reported for this ion in $Na[O_2CH]$.[27] The C(21)–O(1) and C(21)–O(2) distances of 1.218(6) and 1.226(6) Å respectively are not considered to be significantly different,[6] despite the asymmetry in the Cu–O(1) and Cu–O(2) distance involved, ΔO = 0.845 Å, which might reasonably be expected to generate a significant difference in the C(21)–O bond character (*cf.* the co-ordinated nitrate ion[28]). This suggests that both O(1) and O(2) are equally involved in bonding to the copper atom despite the difference in the Cu–O bond distances. This structural situation is paralleled in the other $[Cu(chelate)_2(OXO)]Y$ systems examined to date, see Table 6, were $OXO^- = O_2CH^-$, O_2CMe^-, and ONO^-. The equivalence of the C–O(1) and C–O(2) bond distances is particularly clear in the formate and acetate complexes of Table 6, where accurate bond-length data are available. Significant differences do occur in two of the nitrite complexes (6) and (7), which also involve accurate data, and although there are differences in one of the remaining nitrite complexes (4) the differences are not considered significant, as less accurate data are involved. In all four nitrites the difference involves N–O(1) > N–O(2), as would be predicted if the O(2) atoms were *not* involved in bonding to the copper(II) atom and might suggest that the data for the nitrite complexes are different in behaviour and should not be compared with that of the formate and acetate complexes. The only significant difference in the bonding role of these anions is the O(1)–X–O(2) angle, which is significantly less than 120° (*ca.* 112°) in the nitrite ligands, while this angle is significantly greater than 120° (*ca.* 124°) in the acetate[29] and formate[30] ligands; the two exceptions (5) and (11), Table 6, both involve the OXO^- group on a two-fold special position which may contribute to the observed differences. The difference of the O(1)–X–O(2) angle can be understood in terms of the lone pair–bond pair repulsion of the nitrite ion, which does not exist with the formate and acetate anions, but it is difficult to see w this results in the different relative X–O(1)/X–O(2) bo lengths, as observed in Table 6.

In (1) the O(1)–C(21)–O(2) angle of 126.2° is not considered significantly different from that of 124° observed in Na[O_2CH][30] and the plane of the formate group is reasonably coplanar (5.29°) with the N(2), N(4), O(1) plane, Table 4. Due to the O(1)–C(21)–O(2) bite angle of the formate anion the O(2) atom lies well off the perpendicular to the N(1), N(2), N(3), O(1) plane by 27.1° at a distance of 2.869 Å from the copper atom, a distance that would normally be considered too long to be involved in even weak off-the-*z*-axis co-ordination to the copper atom.

The stereochemistry of (1) is clearly different from the symmetrical elongated rhombic octahedral (4 + 2) chromophore in [Cu(bipy)$_2$(S_3O_6)][31] and [Cu(bipy)$_2$(S_4O_6)][32] or the unsymmetrical elongated rhombic octahedral (4 + 1 + 1*) chromophore of [Cu(bipy)$_2$(ClO_4)$_2$].[33] It has more similarity with the *cis*-distorted octahedral and (4 + 1 + 1*) stereochemistries in Table 5. Within this series a correlation[12] has been established between the ΔN and ΔO values, defined above, as shown in Figure 4 using the numbering of Table 5. Complex (1) has the longest Cu–O(2) bond distance, a value that is only exceeded by one of 2.878 Å in (3). In addition the ΔN value of (1) is relatively low and results in the point for (1) in Figure 4 lying well off the correlation established for the nitrite and acetate complexes [Cu(bipy)$_2$(OXO)]Y. This anomalous position is only exceeded by the data[34] for [Cu(bipy)$_2$(pydca)]·4H_2O, (12) (where pydca = pyridine-2,6-dicarboxylate) the reason for which lies in a geometric factor associated with the OXO group, which forms part of the pyridine-2,6-dicarboxylate anion. In the case of (3), Table 6, the ΔN and ΔO values yield a point in Figure 4 that lies closer to the correlation of Figure 4, but is sufficiently removed to suggest that the nitrite, acetate, and formate anions should not be forced into a single correlation of this type, especially when large Cu–O(2) distances are involved, *i.e.* ΔO values greater than 0.8 Å. This suggests that there may be an upper limit of 0.8 in the ΔO/ΔN correlation.

TABLE 6

[Cu(chelate)$_2$(OXO)]Y systems: ΔN, ΔO, X–O(1), and X–O(2) data (Å)

	Complex	ΔN	ΔO	X–O(Z)	X–O(X)	Significant difference	O(1)–X–O(2)	Ref.
(1)	[Cu(bipy)$_2$(O_2CH)][BF_4]·0.5H_2O	0.097	0.845	1.218(6)	1.226(6)	No	126.2(5)	This work
(3)	[Cu(bipyam)$_2$(O_2CH)][BF_4]	0.147	0.885	1.264(14)	1.258(15)	No	126.7	*a*
(4)	[Cu(bipy)$_2$(ONO)][NO_3]	0.035	0.091	1.234(13)	1.207(13)	No	111.9	3
(5)	[Cu(bipyam)$_2$(ONO)][NO_2]	0.000	0.000	1.255(13)	1.255(13)	No	118.6	*b*
(6)	[Cu(bipy)$_2$(ONO)][BF_4]	0.088	0.346	1.261(7)	1.211(7)	Yes	112.9	12
(7)	[Cu(phen)$_2$(ONO)][BF_4]	0.119	0.525	1.254(6)	1.206(7)	Yes	113.4	17
(8)	[Cu(bipy)$_2$(O_2CMe)][BF_4]	0.176	0.805	1.270(6)	1.252(7)	No	122.2	4
(2)	[Cu(bipy)$_2$(O_2CMe)][ClO_4]·H_2O	0.112	0.617	1.238(5)	1.241(5)	No	122.8	4
(9)	[Cu(bipyam)$_2$(O_2CMe)][NO_3]	0.126	0.644	1.271(9)	1.247(9)	No	125.5	*a*
(10)	[Cu(phen)$_2$(O_2CMe)][ClO_4]	0.032	0.201	1.175(6)	1.166(6)	No	121.7	6
(11)	[Cu(phen)$_2$(O_2CMe)][BF_4]·2H_2O	0.000	0.000	1.233	1.233	No	117.0	7

[a] B. J. Hathaway, unpublished work. [b] P. C. Power and B. J. Hathaway, unpublished work; H. A. Chen and J. P. Fackler, personal communication.

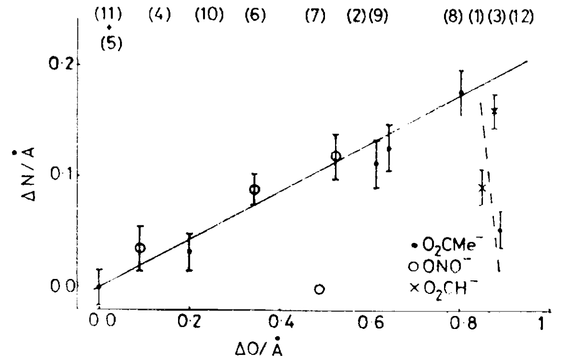

FIGURE 4 Correlation of ΔN, [Cu–N(4)] – [Cu–N(2)], and ΔO, [Cu–O(2)] – [Cu–O(1)] (see Table 6 for compound numbering)

It has already been recognised[2,8] that the sense of the distortion of the regular trigonal-bipyramidal stereochemistry of a [Cu(bipy)$_2$L]Y system, Figure 1(*a*), can take two alternative routes (A) and (B), both of which result in a square-pyramidal distortion, but with the elongation in two different directions, namely, the Cu–L and Cu–N(4) directions, due to the presence of non-equivalent ligands. These differences have been illustrated for a series of cation distortion isomers where L = Cl[8] and L = H_2O.[35] Comparable modes of distortion of the [Cu(bipy)$_2$(OXO)]Y system can be suggested,[12] Figure 1(*b*), involving two alternative modes of co-ordination (C) and (D), the latter of which describes the range of structural situations from symmetrical *cis*-distorted octahedral to a (4 + 1 + 1*) type distortion (D) involving a very asymmetrically bonded OXO^- anion, plus a long Cu–N(4) distance. The present structure of (1) then represents the extreme of this (4 + 1 + 1*) type distorted stereochemistry, arising from the mode IIB vibration of a tris(chelate)copper(II) complex as illustrated in Figure 5 of ref. 11, with the limit of synergic Cu–N(4) elongation and the asymmetric co-ordination of the OXO^- group defined by a ΔO value of 0.8 Å, Figure 4.

Electron Spin Resonance Spectra.—The polycrystalline e.s.r. spectra of both (1) and (2) are rhombic,[16] Figure 3(*b*), with the lowest *g* value only slightly above 2.00. The single-crystal e.s.r. data, Table 5, confirm the rhombic g factors with (1) having an R value[16] [$=(g_2 - g_1)/(g_3 - g_2)$ where $g_3 > g_2 > g_1$] of 0.714, below one and (2) having an R value of 1.41, slightly above one. Both complexes have comparable high g values and almost equal lowest g values of 2.015 and 2.017. The latter are consistent with an approximate d_{z^2} ground state for the CuN_4O chromophore, but with such clearly rhombic, rather than axial g factors, this can not be equated, necessarily, with a trigonal-bipyramidal stereochemistry as both involve a clear (D) type distortion towards square pyramidal. The R value of 0.71 for (1) would suggest that this complex should be more square pyramidal than (2) with an R value of 1.41, a view that is consistent with the larger Cu–O(2) distance of 2.869 Å in (1) compared with that of 2.648 Å in (2), especially as the Cu–N(4) distances of (1) and (2), 2.158(5) and 2.168 Å, respectively, are not significantly different. This also suggests that in these distorted environments the position of the intermediate g factor is a useful pointer to the stereochemistry present; with $g_2 < 2.120$, *i.e.* $R < 1.0$, a long Cu–O(2) distance (>2.70 Å) is involved and with $g_2 > 2.120$, *i.e.* $R > 1.0$, a short Cu–O(2) distance (<2.70 Å) is involved.

In addition to the magnitudes of the g factors in (1) and (2) their directions are also informative; the lowest g factor in both complexes corresponds with the Cu–N(1) direction, to ±11°, and even closer in (1). The intermediate g factor corresponds with the Cu–O(1) direction and the highest g factor with the Cu–N(4) direction to ±5° in (1) but less closely in (2), ± 12° (see later). But even to this accuracy there is a clear correlation between the intermediate and highest g factors with the Cu–O(1) and Cu–N(4) bond directions respectively, Figure 5(*a*) and 5(*b*), than in the case of the more symmetrically bonded OXO^- group in $[Cu(bipy)_2(ONO)][NO_3]$ [11,12] or $[Cu(phen)_2(O_2CMe)][BF_4]\cdot 2H_2O$ [13] (phen = 1,10-phenanthroline) where the intermediate g factor correlates with the bisector of the O(1)–Cu–O(2) angle and the highest g factor lies nearer to the bisector of the O(1)–Cu–N(4) angle, Figure 5(*c*). Consequently, the single-crystal e.s.r. spectra for (1) and (2) establish that, relative to the symmetrical *cis*-distorted octahedral stereochemistry, Figure 1(*b*), the distortion towards square pyramidal along the route (D) pathway results in a significant rotation of the g factors in the plane at right angles to the N(1)–N(3) direction in the sense illustrated in Figure 5. Corresponding with this rotation, there is a characteristic change in the magnitudes of the g values, g_2 decreases, g_3 increases, and g_1 remains invariant. In (4) the R value, 4.5, is clearly greater than 1.0 and consistent with an approximately d_{z^2} ground state, but in (1) and (2) the R values 0.714 and 1.40 respectively are much closer to 1.0 and even suggest for (1) that a $d_{x^2-y^2}$ ground state predominates over a d_{z^2} ground state, with the Cu–N(4) direction the dominant principal axis, rather than the N(1)–N(3) direction. If this is correct, it follows from the numerical values of the single-crystal g factors of (1) and (2), Table 5, that the former has a slightly greater distortion towards square pyramidal than (2), as noted above and consistent with the numerically higher value of g_3 in (1) than in (2), Table 5.

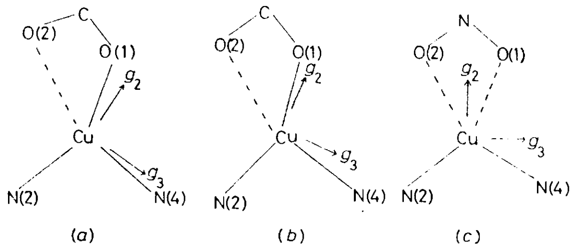

FIGURE 5 The correlation of the local molecular g factors with the Cu–N(4) and Cu–O(1) directions in (*a*) $[Cu(bipy)_2(O_2CH)][BF_4]\cdot 0.5H_2O$; (*b*) $[Cu(bipy)_2(O_2CMe)][ClO_4]\cdot H_2O$, and (*c*) $[Cu(bipy)_2(ONO)][NO_3]$

Some support for this sensitivity of the in-plane g values to the elongation direction in these distorted trigonal-pyramidal chromophores is observed in the values[36] for $[Cu(phen)_2(OH_2)][NO_3]_2$ which has a route (A) distortion,[37] Figure 1(*a*), of a clearly five-coordinate CuN_4O chromophore, Figure 6, but with the in-plane elongation along the Cu–OH_2 direction, 2.18 Å, with $\alpha_3 = 139.6°$. The g values are clearly rhombic with $R = 1.01$, but in this case the ***highest*** g value (2.227) lies along the Cu–OH_2 direction, the principal axis of this C_2 symmetry CuN_4O chromophore, rather than in the direction at right angles as in the CuN_4OH_2 chromophore of $[Cu(bipy)_2(OH_2)][S_5O_6]$.[38]

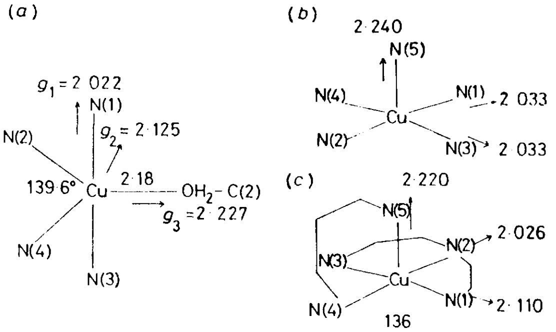

FIGURE 6 Molecular structures and g-factor directions of (*a*) $[Cu(phen)_2(OH_2)][NO_3]_2$, (*b*) $K[Cu(NH_3)_5][PF_6]_3$, and (*c*) $[Cu(dien)(bipyam)][NO_3]_2$

Electronic Spectra.—The electronic spectra of (1) and (2), Figure 3(*a*), consist of two almost equally intense peaks at *ca.* 10 000 and 14 000 cm^{-1}, values that are significantly lower than those previously reported for $[Cu(bipy)_2(O_2CMe)][BF_4]$,[4] 10 860 and 15 150 cm^{-1}, but comparable to those reported[11] for the *cis*-distorted octahedral stereochemistry of $[Cu(bipy)_2(ONO)][NO_3]$, 9 500 and 14 600 cm^{-1}. While the latter has been assigned with a d_{z^2} ground state, the very rhombic g values and the distorted stereochemistry of (1) and (2) make the direction of the g axes uncertain and coupled with the uncertainty of the polarisation directions in the triclinic space group of (1), no attempt was made to measure the polarised single-crystal electronic spectra of these two complexes. Nevertheless, there are differences in the energies of the electronic spectra, Table 7, which should reflect a difference in the tetragonality, T, present (where T is the mean in-plane bond distance/mean out-of-plane bond distance). If the tetragonality is defined with the principal axes in the approximate direction of Cu–N(4) then both a five-co-ordinate (T^5) and a six-co-ordinate (T^6) tetragonality can be calculated, Table 7. As the high electronic energies of [Cu(bipy)$_2$(O$_2$CMe)][BF$_4$] correlate best with the ***unique*** lowest tetragonality T^5, the electronic energies clearly correlate better with T^5, rather than T^6. Thus despite the structural evidence for the involvement of the O(2) atom in weak bonding to the copper ion, the energies of the electronic spectra are determined primarily by the five short-bonded ligands and the electronic consequence of the O(2) ligand is small. Nevertheless the square-pyramidal stereochemistry involved is far from the regular stereochemistry [25] of K[Cu(NH$_3$)$_5$][PF$_6$]$_3$, Figure 6(*b*), which involves almost equal basal angles of 165 ± 1° and yields the axial g values of $g_\perp = 2.033$ and $g_\parallel = 2.240$. It is more comparable to the trigonal distortion of the square-pyramidal stereochemistry [39] of [Cu(dien)(bipyam)][NO$_3$]$_2$ (dien = diethylenetriamine and bipyam = di-2-pyridylamine) where a near trigonal angle of 136°, Figure 6(*c*), is involved and which, in the copper-doped [Zn(dien)(bipyam)][NO$_3$]$_2$ [40] complex, yields closely comparable g factors of $g_1 = 2.026$, $g_2 = 2.110$, and $g_3 = 2.220$. The square-pyramidal stereochemistry of (1) and [Cu(dien)(bipyam)][NO$_3$]$_2$ are characterised by a clear trigonal distortion related in the sense of the Berry twist [9] mechanism, plus a short Cu–N(5) ligand distance of *ca.* 2.15 Å, resulting from an out-of-the-basal-plane chelate ligand restriction, which is significantly shorter than the corresponding distance [25] of 2.193 Å in K[Cu(NH$_3$)$_5$][PF$_6$]$_3$. With this out-of-the-plane bite restriction on the fifth ligand bond length, it is worth considering [41] the electrostatic effect of this lone pair of electrons on the fifth ligand on the electron density in the filled d_{z^2} orbital, Figure 7. In a regular elongated tetragonal-octahedral stereochemistry the distribution will be symmetrical, Figure 7(*a*), with equal electron distribution above and below the copper(II) ion, but the closer approach of a fifth ligand can reduce the electron density above the copper(II) ion and increase it below, Figure 7(*b*), while with very short fifth ligand distances the asymmetric occupation will be very marked, Figure 7(*c*), and is accompanied by a distortion of the copper(II) ion out of the plane of the four equatorial ligands towards the fifth ligand. In this situation, the O(2) atom of a OXO$^-$ ligand is favourably placed for overlap with the expanded d_{z^2} orbital, Figure 7(*d*), not withstanding that the O(2) atom lies at a significant distance from the copper(II) ion, 2.6—2.9 Å, and could result in significant Cu–O(2) bonding. This could account for the near equivalence of the C–O bond distances in the acetate and formates of Table 6, but still fails to account for the difference in the nitrites.

TABLE 7

The electronic reflectance spectral data (cm^{-1}) of (*a*) [Cu(bipy)$_2$(O$_2$CH)][BF$_4$]·0.5H$_2$O, (*b*) [Cu(bipy)$_2$(O$_2$CMe)][ClO$_4$]·H$_2$O, and (*c*) [Cu(bipy)$_2$(O$_2$CMe)][BF$_4$] and their tetragonalities T^5 and T^6, see text for definition

	(*a*)	(*b*)	(*c*)
$d_{z^2} \rightarrow d_{x^2-y^2}$	10 200	9 990	10 860
$d_{xz}d_{yz}d_{xy} \rightarrow d_{x^2-y^2}$	14 360	13 880	15 150
T^5	0.934	0.929	0.908
T^6	0.802	0.836	0.803

If the OXO$^-$ anions in the structures of Figure 2 are involved in a bidentate bonding function irrespective of the separate Cu–O(1) and Cu–O(2) distances, then it is at least understandable why the plot of ΔN against ΔO of Figure 4 covers the range of ΔO values observed, since the precise geometry obtained will be determined by relatively weak forces in the lattice including hydrogen bonding. This flexible co-ordinating role of the OXO$^-$ anion in these [Cu(bipy)$_2$(OXO)]Y systems further demonstrates the flexible stereochemistry of the copper(II) [16,25] ion or plasticity effect [42] due to the non-spherical symmetry of the d^9 configuration of the copper(II) ion and suggests that the [Cu(bipy)$_2$(OXO)]Y systems should be considered as six-co-ordinate, Figure 1(*b*), rather than as five-co-ordinate, Figure 1(*a*), as suggested earlier.[11]

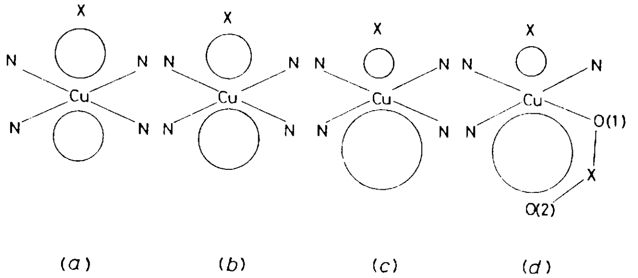

FIGURE 7 The distribution of electron density in the d_{z^2} orbital of a square-pyramidal stereochemistry in different stereochemistries: (*a*) elongated tetragonal octahedral, (*b*) in-plane square pyramidal, (*c*) out-of-plane square pyramidal, (*d*) (*c*) plus off-the-z-axis bonding of an OXO$^-$ anion

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