The Crystal Structure and Electronic Properties of *catena*-Bis-(2,2'-bipyridyl)-μ-tetrafluoroborato-copper(II) Tetrafluoroborate and *catena*-Bis(2,2'-bipyridyl)-μ-perchlorato-copper(II) Perchlorate †

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The crystal structure of $[Cu(bipy)_2(F_2BF_2)][BF_4]$ (3) (bipy = 2,2'-bipyridyl) has been determined by *X*-ray analysis [triclinic, space group $P\bar{1}$, with a = 11.275(4), b = 14.760(5), c = 7.366(3) Å, α = 96.44(3), β = 101.63(4), γ = 110.25(4)°, and Z = 2], and that of $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$ (1) has been redetermined [triclinic, space group $P\bar{1}$, a = 11.238(4), b = 14.863(5), c = 7.403(3) Å, α = 96.28(3), β = 99.49(4), γ = 110.21(4)°, and Z = 2]. The two structures are isomorphous with near isostructural, six-co-ordinate, elongated rhombic *trans* octahedral CuN_4X_2 chromophores. The co-ordination of the bipy ligands is approximately planar, with a tetrahedral twist of the CuN_4 chromophore [dihedral angle 44.6 and 46.7° for (3) and (1), respectively]. The six-co-ordination is completed by one bridging (and one ionic) tetrafluoroborate and perchlorate anions, in (3) and (1), respectively, at non-equivalent copper–ligand distances consistent with semi-co-ordination. The structure of complex (3) represents the first crystallographic example of a bridging tetrafluoroborate anion and the i.r. spectrum at liquid-nitrogen temperature is consistent with this, showing clear splitting of the ν_3 band. The electronic and e.s.r. spectra of the complexes are consistent with their elongated rhombic octahedral stereochemistries and are discussed as a 'criterion of stereochemistry' for this geometry in the structural pathway of $[Cu(bipy)_2X]Y$ complexes.

The original *X*-ray structure [1] determination of $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$ (1) (bipy = 2,2'-bipyridyl) involved photographic data collection and refined to a conventional *R* value of 0.134. The structure involved a bridging perchlorate group with non-equivalent Cu–O bond distances of 2.45 and 2.73 Å, short enough to be consistent with the involvement of the bridging perchlorate group in semi-co-ordination [2] to the copper atom. Despite this structural situation there is no i.r. spectral evidence for the co-ordination of the perchlorate group [3] in this complex. For this reason the crystal structure has been redetermined using diffractometer data collection, the i.r. spectrum has been recorded at low temperature, and the results compared with those for $[Cu(bipyam)(O_2CCH_3)(O_2ClO_2)]\cdot H_2O$ (2) (bipyam = di-2-pyridylamine), which also involves [4] the uncommon bridging semi-co-ordinated perchlorate group. As the original report [3] on $[Cu(bipy)_2(F_2BF_2)][BF_4]$ (3) also suggested an elongated rhombic octahedral CuN_4F_2 chromophore but no i.r. evidence for co-ordinated tetrafluoroborate anions, its crystal structure has also been determined, along with its i.r. spectrum at low temperature.

Experimental

Complexes (1)—(3) were prepared as previously described [3,4] and characterised by microanalysis.

Crystallography.—Table 1 lists the crystal and refinement data for complexes (1) and (3).‡ The unit-cell dimensions were determined and refined on a Philips PW1100 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 the acceptance criterion of $I > 2.5\sigma(I)$, 3 265 reflections were retained for complex (3) and 3 457 for (1). Lorentz and polarisation corrections were applied, but no corrections were made for absorption. The structures were solved by Patterson and Fourier techniques, and refined by blocked-matrix least squares with anisotropic thermal parameters for all of the non-hydrogen atoms. In (3) the bridging tetrafluoroborate anion had reasonable thermal parameters,[7] but those of the ionic BF_4^- anion were rather high (maximum 0.37 $Å^2$). Attempts to refine the ionic BF_4^- as a disordered anion failed to lower the anisotropic thermal parameters, consequently the ionic BF_4^- was refined as an ordered model, when the highest residual electron density (0.75 e $Å^{-3}$) was then associated with the copper atom and not with the ionic BF_4^- anion. In (1) the bridging ClO_4^- anion involved reasonable anisotropic thermal parameters, but those of the ionic ClO_4^- anion were high [8] and the maximum residual electron density was associated with this ClO_4^- anion. For this reason the ionic ClO_4^- was refined as a disordered group with three additional oxygen atoms O(6'), O(7'), O(8') (s.o.f. 0.47, 0.36, and 0.31, respectively), which were included with linked site occupation factors (s.o.f.s) relative to those for the corresponding O(6), O(7), and O(8). This procedure still resulted in some high anisotropic thermal parameters,[8] but these were still lower than those obtained for the ordered ClO_4^- anion.

† *Supplementary data available* (No. SUP 23692, 61 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, least-squares planes, structure factors for (1) and (3); atomic co-ordinates for (1). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ The original data [1] for (1) were collected using the following unit-cell data: a = 7.44, b = 14.93, c = 15.32 Å, α = 136.3, β = 103.7, and γ = 83.2°. When first recollected, the unit cell for (1) was a = 7.403, b = 11.238, c = 14.863 Å, α = 110.21, β = 96.28, and γ = 99.49°, involving a transformation matrix [5] [$\bar{1}$00, 0$\bar{1}$1, 0$\bar{1}$0] and that for (3) was a = 7.366, b = 11.275, c = 15.158 Å, α = 114.00, β = 105.02, and γ = 78.37°. In order to establish the isomorphous relationship between (1) and (3) these unit cells were subjected to Delauny reduction [6] to obtain the reduced unit cells, transformation matrix [001, 100, 010] and [010, 0$\bar{1}\bar{1}$, $\bar{1}$00] for (3) and (1), respectively, and the structures were solved in these reduced unit cells, Table 1.

Table 1. Crystal and refinement data

Compound	(1) $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$	(3) $[Cu(bipy)_2(F_2BF_2)][BF_4]$
M_r	574.66	538.37
Stoicheiometry	$C_{20}H_{16}Cl_2CuN_4O_8$	$C_{20}H_{16}B_2CuF_8N_4$
a/Å	11.238(4)	11.275(4)
b/Å	14.863(5)	14.760(5)
c/Å	7.403(3)	7.366(3)
α/°	96.28(3)	96.44(3)
β/°	99.49(4)	101.63(4)
γ/°	110.21(4)	110.25(4)
U/Å^3	1 125.9	1 104.13
D_m(flotation)/g cm^{-3}	1.68(2)	1.60(2)
D_c/g cm^{-3}	1.65	1.62
$F(000)$	581.98	549.98
μ/cm^{-1}	12.06	10.25
No. of unique reflections	3 457	3 265
$R = (\Sigma\Delta/\Sigma\|F_o\|)$	0.0590	0.0507
$R' = (\Sigma\Delta w^{\frac{1}{2}}/\Sigma\|F_o\|w^{\frac{1}{2}})$	0.0666	0.0604
k	1.9393	1.000
g	0.000 781	0.001 12
Maximum final shift/e.s.d.	0.05	0.02

Data common to both compounds: space group, $P\bar{1}$; $Z = 2$; Mo-K_α radiation, $\lambda = 0.710\,69$ Å; residual electron density, 0.75 e Å^{-3}.

Table 2. Fractional atomic co-ordinates for complex (3)

Atom	x	y	z	Atom	x	y	z
Cu	0.378 63(4)	0.238 78(3)	0.098 63(6)	N(3)	0.545 8(3)	0.353 9(2)	0.139 2(4)
N(1)	0.217 0(3)	0.123 7(2)	−0.035 2(4)	C(11)	0.656 9(4)	0.352 6(4)	0.107 4(7)
C(1)	0.108 6(4)	0.127 1(3)	−0.148 9(6)	C(12)	0.767 9(5)	0.434 9(5)	0.142 9(8)
C(2)	0.008 5(4)	0.042 1(3)	−0.256 8(6)	C(13)	0.762 8(6)	0.524 7(5)	0.214 7(8)
C(3)	0.020 2(4)	−0.046 3(3)	−0.252 7(6)	C(14)	0.647 4(5)	0.528 6(4)	0.240 4(7)
C(4)	0.131 4(4)	−0.050 4(3)	−0.138 1(6)	C(15)	0.537 8(4)	0.441 0(3)	0.200 8(5)
C(5)	0.228 6(3)	0.037 1(3)	−0.030 3(5)	C(16)	0.408 7(5)	0.435 2(3)	0.219 1(5)
C(6)	0.352 0(4)	0.041 6(3)	0.091 7(5)	C(17)	0.381 8(7)	0.516 3(4)	0.290 2(6)
C(7)	0.374 3(4)	−0.040 6(3)	0.139 5(6)	C(18)	0.254 3(7)	0.501 0(4)	0.301 2(7)
C(8)	0.492 3(5)	−0.027 8(3)	0.258 9(6)	C(19)	0.162 8(6)	0.411 3(4)	0.248 8(7)
C(9)	0.583 5(5)	0.065 0(4)	0.327 3(6)	C(20)	0.194 1(5)	0.334 0(3)	0.180 0(6)
C(10)	0.558 0(4)	0.145 3(3)	0.279 6(5)	N(4)	0.312 8(3)	0.345 2(2)	0.163 4(4)
N(2)	0.442 7(3)	0.132 6(2)	0.158 1(4)	B(2)	0.132 8(7)	0.718 2(5)	0.237 6(15)
B(1)	0.337 2(4)	0.209 2(3)	0.575 1(6)	F(5)	0.258 8(4)	0.738 3(3)	0.290 1(7)
F(1)	0.406 0(3)	0.232 3(2)	0.761 3(4)	F(6)	0.063 4(4)	0.624 4(4)	0.198 2(12)
F(2)	0.418 6(3)	0.261 6(2)	0.471 6(3)	F(7)	0.119 5(6)	0.744 7(4)	0.055 4(10)
F(3)	0.293 0(3)	0.111 0(2)	0.507 7(5)	F(8)	0.093 8(8)	0.774 4(6)	0.328 5(16)
F(4)	0.231 3(3)	0.238 2(2)	0.559 5(5)				

The positions of the hydrogen atoms were calculated geometrically and floated on the associated carbon atoms, assuming C–H 1.08 Å and a fixed thermal parameter of 0.07 Å^2. The refinements converged when the shift-to-error ratio of any parameter was less than 0.02 and 0.05 for (3) and (1), respectively, with a refined weighting scheme, $w = k/[\sigma(F_o) + g(F_o)^2]$, the final values of k and g being given in Table 1. Complex atomic scattering factors [9] were employed and the Cu and Cl atoms were corrected for anomalous dispersion.

All calculations were carried out using the SHELX 76 [10] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and PRETAB (K. Henrick) system of programs on an IBM 4341 and VAX 11/780 computer. The final atomic co-ordinates for complex (3) are given in Table 2 and those for (1) are in SUP 23692. Table 3 gives selected bond lengths and angles and Table 4 some relevant mean plane data. Figure 1 illustrates the structure of (1) and (3), viewed approximately parallel to the a axis, and the atom-numbering scheme used.

Spectroscopic Properties.—These were recorded as previously described; [11] the low-temperature i.r. spectra were determined using a RIIC low-temperature attachment, and recorded on a Perkin-Elmer 257 spectrometer. Figure 2 shows the electronic reflectance spectra of complexes (1) and (3), Figure 5 the i.r. spectra (900—1 300 cm^{-1}) at room temperature and at liquid-nitrogen temperature.

Results and Discussion

Crystal Structures.—The structure of complex (3) consists of chains of $[Cu(bipy)_2(F_2BF_2)]^+$ cations, parallel to the a axis, and BF_4^- anions. The structure of the cation involves a six-co-ordinate elongated rhombic octahedral CuN_4F_2 chromophore. The two bipy ligands bond nearly symmetrically in the plane, mean Cu–N distance 1.99 Å, with fluorine atoms from the bridging BF_4^- groups occupying the fifth and sixth co-ordination positions at significantly different bond distances, 2.560(5) and 2.656(5) Å, respectively, both of which are within the distance (2.7 Å) normally associated with semi-co-ordination [2] of the BF_4^- anion. There are no unusual bond lengths or bond angles in the bipy ligands [12] which are reasonably planar, with angles of twist between the pyridine rings of 10.1 and 2.8°, respectively, within the range normally

Table 3. Selected bond lengths (Å) and angles (°)

	[Cu(bipy)$_2$-(F_2BF_2)][BF_4] (3)		[Cu(bipy)$_2$-(O_2ClO_2)][ClO_4] (1)		[Cu(bipy)$_2$-(F_2BF_2)][BF_4] (3)		[Cu(bipy)$_2$-(O_2ClO_2)][ClO_4] (1)
Cu–N(1)	1.948(2)		1.988(4)	N(1)–Cu–N(2)	81.8(1)		81.8(2)
Cu–N(2)	1.994(4)		1.996(4)	N(1)–Cu–N(3)	159.6(1)		161.8(2)
Cu–N(3)	1.993(3)		1.984(4)	N(2)–Cu–N(3)	101.8(1)		102.0(2)
Cu–N(4)	2.007(4)		2.005(4)	N(1)–Cu–N(4)	103.7(1)		103.5(2)
Cu–F(1)	2.560(5)	Cu–O(1)	2.512(5)	N(2)–Cu–N(4)	153.5(1)		151.8(2)
Cu–F(2)	2.656(5)	Cu–O(2)	2.746(5)	N(3)–Cu–N(4)	82.2(1)		81.7(2)
B(1)–F(1)	1.372(5)	Cl(1)–O(1)	1.418(4)	F(1)–B(1)–F(2)	108.6(3)	O(1)–Cl(1)–O(2)	108.4(3)
B(1)–F(2)	1.395(6)	Cl(1)–O(2)	1.438(4)	F(1)–B(1)–F(3)	110.7(4)	O(1)–Cl(1)–O(3)	109.6(3)
B(1)–F(3)	1.354(5)	Cl(1)–O(3)	1.412(4)	F(1)–B(1)–F(4)	109.2(4)	O(1)–Cl(1)–O(4)	109.2(3)
B(1)–F(4)	1.390(7)	Cl(1)–O(4)	1.425(5)	F(2)–B(1)–F(3)	110.8(4)	O(2)–Cl(1)–O(3)	111.0(3)
B(2)–F(5)	1.310(9)	Cl(2)–O(5)	1.385(1)	F(2)–B(1)–F(4)	108.3(4)	O(2)–Cl(1)–O(4)	110.3(3)
B(2)–F(6)	1.298(8)	Cl(2)–O(6)	1.421(12)	F(3)–B(1)–F(4)	109.2(3)	O(3)–Cl(1)–O(4)	108.4(3)
B(2)–F(7)	1.432(8)	Cl(2)–O(7)	1.331(14)				
B(2)–F(8)	1.256(15)	Cl(2)–O(8)	1.351(12)				

Table 4. Summary of some relevant mean plane data (root-mean-square deviations in Å) for [Cu(bipy)$_2$(F_2BF_2)][BF_4] and [Cu(bipy)$_2$-(O_2ClO_2)][ClO_4]

Plane	[Cu(bipy)$_2$(F_2BF_2)][BF_4]	[Cu(bipy)$_2$(O_2ClO_2)][ClO_4]
(1) N(1), C(1)–C(5)	0.0040	0.0064
(2) N(2), C(6)–C(10)	0.0080	0.0037
(3) N(1), C(1)–C(10), N(2)	0.0865	0.1173
(4) N(3), C(11)–C(15)	0.0144	0.0114
(5) N(4), C(16)–C(20)	0.0065	0.0155
(6) N(3), C(11)–C(20), N(4)	0.0283	0.0378
(7) N(1)–N(4)	0.4048	0.4008
Dihedral angles (°) between planes		
(1)–(2)	10.09	13.86
(4)–(5)	2.77	3.74
(3)–(6)	44.6	46.69

found [12] for the bipy ligand. The mean planes of the bipy ligands involve a tetrahedral CuN_4 chromophore, with a dihedral angle of 44.6°. There is no disorder [7] associated with the nearly symmetrically bridging BF_4^- anion, which is almost regular tetrahedral, mean B–F distance 1.378 Å and mean angles 109.5°. The bridging BF_4^- anion of complex (3) is unique in terms of crystallographic evidence for this mode of co-ordination, although it is believed [13] to occur in $SnMe_3$-(F_2BF_2). The ionic BF_4^- anion of complex (3) exhibits high thermal parameters,[7] and consequently the B–F distances are short (mean 1.34 Å).

The structure of complex (1) involves an elongated rhombic octahedral CuN_4O_2 chromophore with a bridging ClO_4^- anion, Figure 1, and is isostructural with that of (3). It is not significantly different from that previously reported,[1] but is more accurately determined; the bridging ClO_4^- is almost regular tetrahedral, mean Cl–O distance 1.43 Å and mean O–Cl–O angle 109.5° (Table 3). The bridging role of the ClO_4^- anion [14] with *short* metal–oxygen distances is reasonably well established, while at *long* Cu–O distances,[15] mean 2.63 Å, it has only been characterised once before [16] in [Cu(bipyam)(O_2CCH_3)(O_2ClO_2)]·H_2O (2) with Cu–O distances of 2.54 and 2.64 Å, respectively. In complex (2) the bridging ClO_4^- anion is subject to some disorder, consequently the bridging anion in (1) is considered to involve a better defined bridging semi-co-ordinate ClO_4^- anion.

Electronic Properties.—The polycrystalline e.s.r. spectra of complexes (1) and (3) have been reported previously; [3] both involve axial spectra with lowest g values of 2.050 and 2.049, respectively, but with the high g values poorly defined. The single-crystal g values are more informative, Table 5, and yield near-axial spectra with a small rhombic component, consistent with the elongated rhombic octahedral [11] CuN_4X_2 chromophores. For complex (1) the highest g value lies parallel to the approximate a axis, Table 5, and to the elongation axis of the CuN_4O_2 chromophore, and the in-plane g values correspond with the N(1)–N(3) and N(2)–N(4) directions, consistent with a $d_{x^2-y^2}$ rather than a d_{xy} ground state, due to the tetrahedral twist of the in-plane CuN_4 chromophore. The $d_{x^2-y^2}$ ground state for (3) is consistent with the $d_{x^2-y^2}$ ground state previously determined [17] for [Cu(bipyam)$_2$][ClO_4]$_2$ (4), which has a compressed tetrahedral CuN_4 chromophore [18] (dihedral angle 55.6°), but no long fifth or sixth bond distances.

The electronic reflectance spectra of complexes (3) and (1) involve single broad peaks at 15 200 and 15 100 cm^{-1}, respectively, as previously reported,[3] with no evidence of a shoulder to high or low frequency. Consequently, all four d–d transitions (d_{z^2}, d_{xy}, d_{xz}, and $d_{yz} \longrightarrow d_{x^2-y^2}$) are presumed to lie within the band envelope at 15 150 cm^{-1} for both complexes.[11] The observation of a single peak in the electronic spectra of (1) and (3) at *ca.* 15 150 cm^{-1} is consistent with the single peak at *ca.* 14 800 cm^{-1} observed in the spectra of [Cu(bipy)$_2$(S_3O_6)] and [Cu(bipy)$_2$(S_4O_6)], both of which [19] involve an elongated rhombic octahedral CuN_4O_2 chromophore with a marked tetrahedral twist of the bipy ligands, Table 6, and comparable tetragonalities (T = mean in-plane Cu–N distance/mean out-of-plane Cu–O distance). All four complexes involve near-axial e.s.r. spectra, Table 6, with $g_3 \gg g_2 \approx g_1 > 2.0$ [$R = (g_2 - g_1)/(g_3 - g_2) \ll 1.0$], and establish an electronic criteria of stereochemistry [20] for the elongated rhombic

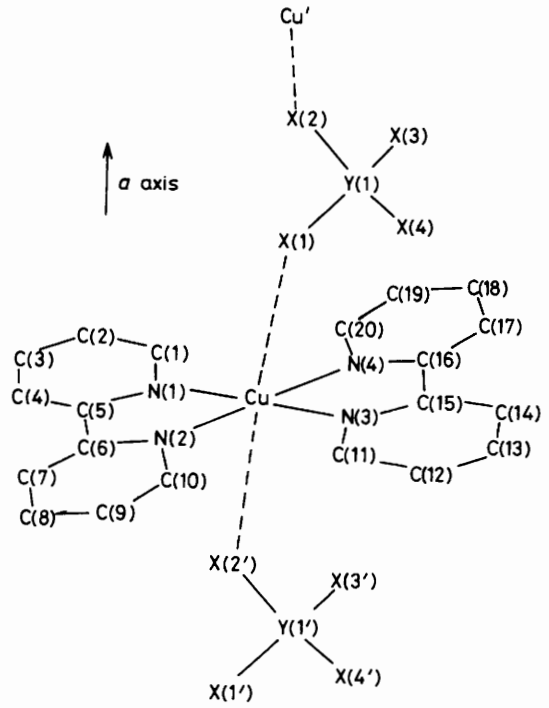

Figure 1. The molecular structures of $[Cu(bipy)_2(X_2YX_2)][YX_4]$ and the atom-numbering scheme used, viewed approximately along the *a* axis

Table 5. The single-crystal *g* values of complexes (1) and (3) along with the direction cosines for (3) and those of the relevant copper–ligand directions measured with respect to the *l*, *m*, and *n* directions on the 1$\bar{1}$0 face; *l* parallel to the *c* axis, *n* perpendicular to the 1$\bar{1}$0 face

	$[Cu(bipy)_2(O_2ClO_2)][ClO_4]$			$[Cu(bipy)_2(F_2BF_2)][BF_4]$
	l	*m*	*n*	
g_3(2.255)	6	87	83	2.243
g_2(2.065)	89	25	115	2.070
g_1(2.054)	97	65	25	2.055
O(1)–O(2)	10	92	87	
N(1)–N(3)	89	123	57	
N(2)–N(4)	102	65	27	

octahedral CuN_4X_2 chromophore of the $[Cu(bipy)_2X]Y$ systems; this stereochemistry can thus be distinguished (Figure 2) from that of a trigonal distorted square-pyramidal CuN_4O chromophore [21] as in $[Cu(bipy)_2(OH_2)][S_2O_6]$, Figure 3(*a*), which has a single peak at a significantly lower energy of 12 450 cm^{-1} (Figure 2) and *g* values of 2.011, 2.158, and 2.225 ($R = 2.19$) consistent with a d_{z^2} ground state,[11] $g_3 \sim g_2 \gg g_\parallel \approx 2.0$. Equally it can be distinguished from a tetrahedral CuN_4 chromophore [22] as in $[Cu(bipy)_2][PF_6]_2$, Figure 2(*c*), which has a band maximum at 15 040 cm^{-1} with a clear high-energy shoulder at 16 950 cm^{-1} and axial *g* values of 2.06 and 2.253 ($R \gg 1.0$), consistent [11] with a $d_{x^2-y^2}$ ground state ($g_\parallel \gg g_\perp > 2.0$). Taken together (Figure 4), these electronic properties offer [20] an ' electronic criterion of stereochemistry ' for the trigonal distorted square-pyramidal, elongated rhombic octahedral, and tetrahedral stereochemistries in this related series of $[Cu(bipy)_2X]Y$ complexes, which are linked [23] in the partial structural pathway [24] of Figure 3.

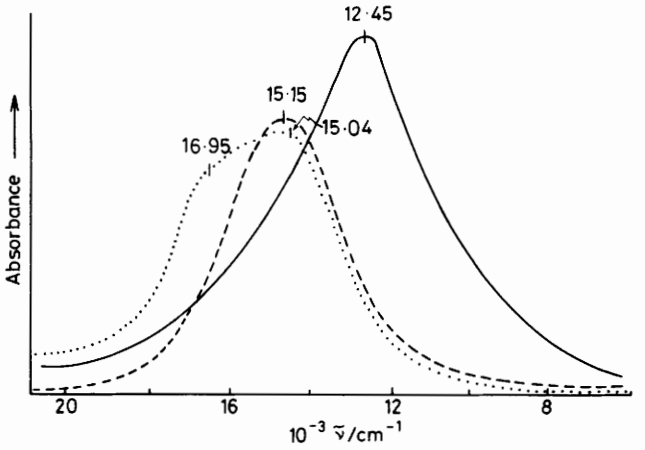

Figure 2. The electronic reflectance spectra of $[Cu(bipy)_2(F_2BF_2)][BF_4]$ and $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$ (- - -), $[Cu(bipy)_2(OH_2)][S_2O_6]$ (—), and $[Cu(bipy)_2][PF_6]_2$ (· · ·)

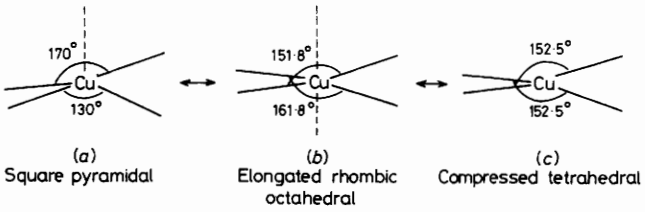

Figure 3. Molecular structures and structural pathway of (*a*) $[Cu(bipy)_2(OH_2)][S_2O_6]$, (*b*) $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$, and (*c*) $[Cu(bipy)_2][PF_6]_2$

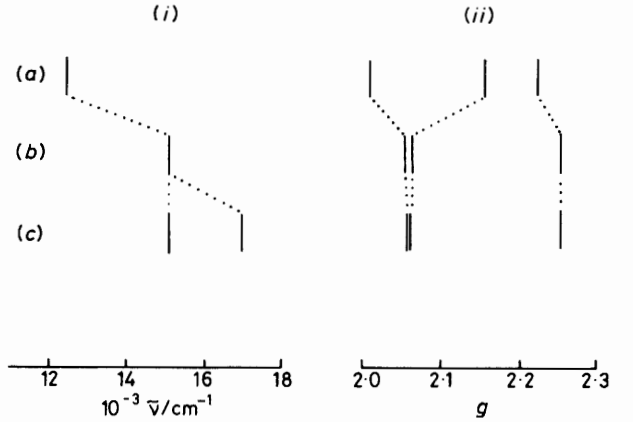

Figure 4. Correlation of the electronic properties of the $[Cu(bipy)_2X]Y$ complexes in Figure 3 along the structural pathway (*a*)—(*c*) (Figure 3): (*i*) electronic spectra; (*ii*) e.s.r. spectra

Infrared Spectra.—Due to overlapping peaks from the bipy ligands present only the ν_3 band of a tetrahedral ClO_4^- and BF_4^- ion were clearly resolved, Figure 5(*a*) and (*b*). At room temperature complex (1) gives a single peak [2] at 1 082 cm^{-1}, while (3) gives a broader peak split into two peaks at 1 030 and 1 070 cm^{-1} with a poorly resolved shoulder at 1 105 cm^{-1}. At the temperature of liquid nitrogen the band of (1) at 1 082 cm^{-1} is just resolved into two peaks at 1 079 and 1 095 cm^{-1}, while that of (3) is more clearly resolved into three peaks at 1 030, 1 070, and 1 105 cm^{-1}.

These i.r. bands are assigned as the triply degenerate ν_3 mode of vibration of the tetrahedral ClO_4^- and BF_4^- ion in

Table 6. Structural and electronic data for some six-co-ordinate CuN_4O_2 chromophores

Complex	Chromophore	Co-ordination number	bipy dihedral angle (°)	Tetragonality, T	Band maximum (cm^{-1})	Single-crystal e.s.r. spectrum g_1	g_2	g_3
$[Cu(bipy)_2(S_4O_6)]$ [19]	CuN_4O_2	6	56.3	0.76	14 700	2.062	2.067	2.228
$[Cu(bipy)_2(S_3O_6)]$ [19]	CuN_4O_2	6	—	0.71	14 900	2.054	—	—
$[Cu(bipy)_2(O_2ClO_2)][ClO_4]$	CuN_4O_2	6	46.7	0.757	15 100	2.054	2.065	2.255
$[Cu(bipy)_2(F_2BF_2)][BF_4]$	CuN_4F_2	6	44.6	0.763	15 200	2.055	2.070	2.243
$[Cu(bipy)_2(OH_2)][S_2O_6]$ [21]	CuN_4O	5	—	—	12 450	2.011	2.158	2.225
$[Cu(bipy)_2][PF_6]_2$ [22]	CuN_4	4	44.6	—	15 040, 16 950	2.06	—	2.253

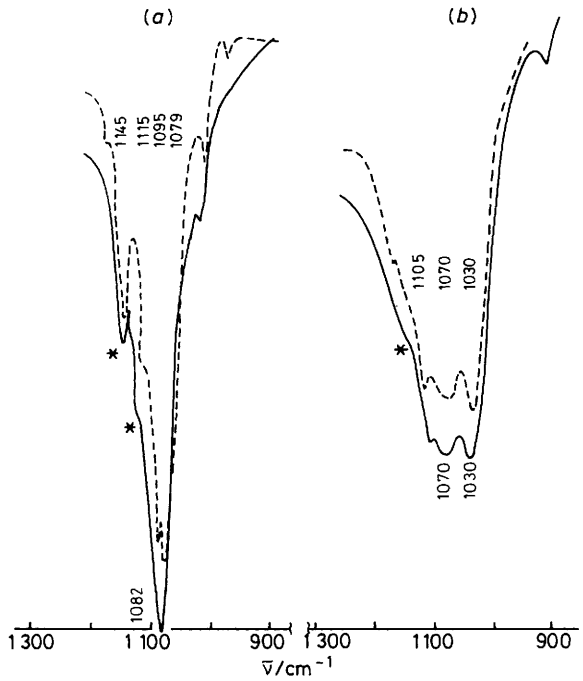

Figure 5. The i.r. spectra (900—1 300 cm^{-1}) of (*a*) $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$ and (*b*) $[Cu(bipy)_2(F_2BF_2)][BF_4]$: recorded at 298 (——) and 77 K (– – –); absorptions marked with an asterisk are due to bipy

(1) and (3), respectively, bands which can be resolved into two or three bands [2,14] when these anions are involved in unidentate co-ordination (C_{3v}) or bidentate co-ordination (C_{2v}), respectively. In the ionic perchlorate this results [25] in splitting into three bands at 1 030, 1 130, and 1 270 cm^{-1}, with ν_1 appearing strongly at 920 cm^{-1}. From Figure 5(*a*) the single sharp peak at 1 082 cm^{-1} at room temperature, the small splitting of 16 cm^{-1} at liquid-nitrogen temperature, and the absence of any intensity of the ν_1 band at 920 cm^{-1} all suggest that the ClO_4^- anion in complex (1) is ionic (as previously suggested [2]) and not co-ordinated.[26] This interpretation contrasts with the clear bridging role of the $Cl(1)O_4^-$ perchlorate in (1), which has near C_{2v} symmetry, notwithstanding the relatively short Cu–O(1) and Cu–O(2) distances of 2.512 and 2.746 Å respectively, and shows no evidence for disorder. These distances are consistent with semi-co-ordination [2] of the ClO_4^- anion, evidence for which should appear in the i.r. spectrum as previously established [2] for this anion in $[Cu(en)_2(OClO_3)_2]$ (en = ethylenediamine). Even if the two bands at 1 115 and 1 145 cm^{-1} were assigned as arising from the perchlorate group and not due to the bipy ligand (they could only be assigned as two of the three components of ν_3, with the third component lying under the intense band at 1 082 cm^{-1} of the ionic ClO_4^-) it is surprising that there is no evidence for the forbidden ν_1 band at 930 cm^{-1}, which becomes allowed in the lower symmetry of C_{3v} or C_{2v}, and appears [25] with 30—40% intensity in the spectrum of $[Cu(en)_2(OClO_3)_2]$ (see Figure 4, ref. 2). The total absence of any indication for even a weak band at 930 cm^{-1} casts serious doubt on this alternative assignment. The total absence of any i.r. evidence for the bridging role of the ClO_4^- ion in complex (1) is not understood.

In contrast,[3] the ν_3 band of the BF_4^- ion in complex (3) at *ca.* 1 100 cm^{-1} is clearly split into three peaks, especially at low temperature, consistent with the bridging role of the BF_4^- anion in approximate C_{2v} symmetry. The Cu–F(1) and Cu–F(2) distances of 2.560 and 2.656 Å, respectively, are consistent with semi-co-ordination [2] of the BF_4^- anions to the copper(II) ions, as established [27] for the BF_4^- ion in $[Cu(en)_2(FBF_3)_2]$ with a Cu–F distance of 2.56 Å. The BF_4^- anion is normally considered to have a negligible function as a co-ordinating anion [28] due to the high electronegativity of the fluorine atoms [29] involved and generally exists as an ionic tetrahedral anion.[7] The first i.r. evidence for co-ordination of the BF_4^- anion as a unidentate anion [30] was in $Mn(MeCN)_4(FBF_3)_2$ and $Zn(MeCN)_4(FBF_3)_2$ and as a bidentate anion [13] in $SnMe_3(F_2BF_2)$, at which time no *X*-ray crystallographic evidence was available to support these suggestions. Crystallographic evidence for the unidentate co-ordination of BF_4^- is limited to $[Ni(en)_2(OH_2)(FBF_3)][BF_4]$,[31] (Ni–F 2.12 Å), $[Cu(FBF_3)(PPh_3)_3]$ [32] (2.31 Å), and $[Cu(na)_2(OH_2)_2(FBF_3)_2]$ (na = nicotinamide) [33] (2.48 Å). The nickel complex [31] shows significant splitting of the ν_3 band (975, 1 015, and 1 090 cm^{-1}) and ν_1 appears with medium intensity at 765 cm^{-1} consistent with the short Ni–F bond distance. The copper(I) complex [31] showed no i.r. evidence for even semi-co-ordination of BF_4^-, despite the relatively short Cu–F distance. No i.r. spectra were reported for the nicotinamide complex.[33] The i.r. spectrum [2] of the semi-co-ordinated BF_4^- anion of $[Cu(en)_2(FBF_3)_2]$ (Cu–F 2.56 Å) shows ν_3 split into two peaks 1 070 and 1 110 cm^{-1}, with a weak shoulder at 1 037 cm^{-1}, and ν_1 at 770 cm^{-1} and ν_2 at 353 cm^{-1} appear with *ca.* 40% intensity. Crystallographic evidence for a semi-co-ordinated BF_4^- anion has also been reported [34] for $[Cu(dth)_2(FBF_3)_2]$ (dth = 2,5-dithiahexane), but no i.r. data were given.

The structural and i.r. data for the co-ordinated BF_4^- anion are summarised in Table 7, which shows that complex (3) exhibits the first crystallographic and i.r. evidence for a low-symmetry bridging semi-co-ordinated $F_2BF_2^-$ anion. Nevertheless, the failure to obtain any i.r. evidence for the bridging semi-co-ordinated ClO_4^- anion in (1) and the co-ordination of the BF_4^- anion in $[Cu(FBF_3)(PPh_3)_3]$ [32] suggests caution in the application of i.r. spectra as a criterion of co-ordination of the ClO_4^- and BF_4^- anions.

Table 7. Crystallographic (Å) and i.r. spectral (cm^{-1}) evidence for co-ordinated BF_4^- anions

Complex	Bonding role	Cu–F	B–F			
$[Ni(en)_2(OH_2)(FBF_3)][BF_4]$ [31]	'Co-ordinated'	2.12(1) (Ni–F)	1.41(1) [a]	1.37(1)	1.36(1)	1.39(1)
			1.27(3)	1.30(2)	1.31(2)	1.35(2)
$[Cu(FBF_3)(PPh_3)_3]$ [32]	'Weakly co-ordinated'	2.31	1.391	1.352	1.391	1.352
$[Cu(en)_2(FBF_3)_2]$ [2]	'Semi-co-ordinated'	2.56	1.41(3) [a]	1.37(2)	1.30(3)	1.38(3)
$[Cu(na)_2(OH_2)(FBF_3)][BF_4]$ [33]	'Semi-co-ordinated'	2.48	—	—	—	—
$[Cu(dth)_2(FBF_3)_2]$ [34,d]	'Semi-co-ordinated'	2.579(5)	1.346(9)	1.374(9)	1.312(9)	1.380(10)
$[Cu(bipy)_2(F_2BF_2)][BF_4]$	'Bridging semi-co-ordinated'	2.560(5) 2.656(5)	1.372(5) [a]	1.395(6)	1.354(5) [a]	1.390(7)
$SnMe_3(F_2BF_2)$ [13,g]	Bridging	—	—	—	—	—
$Mn(MeCN)_4(FBF_3)_2$ [30,g]	Unidentate	—	—	—	—	—
$Zn(MeCN)_4(FBF_3)_2$ [30,g]	Unidentate	—	—	—	—	—

Complex	ν_1	ν_2	ν_3	ν_4
$[Ni(en)_2(OH_2)(FBF_3)][BF_4]$ [31]	765m(sh)	—	975, 1 015, 1 090	516, 521(sh)
$[Cu(FBF_3)(PPh_3)_3]$ [32]	[b] 769	353	984	524
	[c] 769	353	1 016	529
$[Cu(en)_2(FBF_3)_2]$ [2]	770(40%)	355 (40%)	1 037(sh), 1 070, 1 110	521
$[Cu(na)_2(OH_2)(FBF_3)][BF_4]$ [33]	—	—	—	—
$[Cu(dth)_2(FBF_3)_2]$ [34,d]	—	—	—	—
$[Cu(bipy)_2(F_2BF_2)][BF_4]$	—	—	[e] 1 030, 1 070	—
	—	—	[f] 1 030, 1 070, 1 105	
$SnMe_3(F_2BF_2)$ [13,g]	758vs	—	1 005, 1 085, 1 170	—
$Mn(MeCN)_4(FBF_3)_2$ [30,g]	765(sh)	—	973, 1 035—1 085, 1 308m	—
$Zn(MeCN)_4(FBF_3)_2$ [30,g]	765m	—	975, 1 091—1 174, 1 310m	—

[a] Co-ordinated F atom. [b] $^{11}BF_4$. [c] $^{10}BF_4$. [d] No i.r. data available. [e] Room temperature. [f] Low temperature. [g] No crystallographic data available.

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