The Crystal Structure and Electronic Properties of Bis(2,2'-bipyridyl)copper(II) Bis(hexafluorophosphate) †

Judy Foley, Suresh Tyagi, and Brian J. Hathaway *
The Chemistry Department, University College, Cork, Ireland

The crystal structure of the title compound, $[Cu(bipy)_2][PF_6]_2$ (1), has been determined by *X*-ray crystallographic methods, using diffractometer data collection; the structure was solved by the heavy-atom method and by successive Fourier syntheses. Compound (1) crystallises in the tetragonal space group $I4_1/acd$, $a = 16.228(3)$, $c = 18.954(3)$ Å, $Z = 8$; 319 unique reflections gave a final $R = 0.0487$. The structure of (1) involves a unique compressed tetrahedral CuN_4 chromophore (dihedral angle 44.6°) with four additional non-bonding PF_6^- anions at 3.3 Å. The e.s.r. spectrum is axial ($g_{\parallel} \gg g_{\perp} > 2.0$) and the dark green crystals have an electronic reflectance spectrum with a band maximum at 15 040 cm^{-1} with a high-frequency shoulder at 16 950 cm^{-1}. This represents the highest electronic transition yet observed in the $[Cu(bipy)_2X]Y$ type complexes and establishes an 'electronic criterion of stereochemistry' for the compressed tetrahedral CuN_4 chromophore.

Of the $[Cu(bipy)_2X]Y$ (bipy = 2,2'-bipyridyl) type complexes of the copper(II) ion, at least 34 have been characterised crystallographically; [1-4] their stereochemistries are dominated by five- and six-co-ordinate geometries involving a wide range of intermediate distorted geometries.[1-3] In these structures the CuN_4 chromophores generally involve a trigonal or tetrahedral distortion from planar, but to date no example of four-co-ordinate square coplanar or regular tetrahedral geometry has been observed. In an attempt to prepare a bridging PF_6^- anion complex of copper(II), the complex $[Cu(bipy)_2][PF_6]_2$ (1) was prepared as dark green crystals, and its properties have been determined.[5]

Experimental

Preparation.—Copper(II) nitrate trihydrate (0.10 g, 0.4 mmol) and 2,2'-bipyridyl (0.26 g, 1.67 mmol) were dissolved in methanol–water (1 : 3 v/v, 400 cm^3) and a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 g) and KPF_6 (0.9 g, 4.89 mmol) in methanol–water (1 : 1 v/v, 400 cm^3) added. The solution was boiled, filtered, and allowed to evaporate slowly; after 2 d a mixture of blue and dark green crystals was deposited [Found (for the dark green crystals): C, 36.35; H, 2.7; Cu, 8.8; N, 8.35. $C_{20}H_{16}CuF_{12}N_4P_2$ requires C, 36.05; H, 2.4; Cu, 9.55; N, 8.4%].

Crystal Data.—$C_{20}H_{16}CuF_{12}N_4P_2$, $M = 665.504$, Tetragonal, space group $I4_1/acd$, $a = 16.228(3)$, $c = 18.954(3)$ Å; $U = 4\,991.78$ Å^3, $D_m = 1.75 \pm 0.02$, $Z = 8$, $D_c = 1.771$ g cm^{-3}, $F(000) = 2\,647.92$, Mo-K_{α} radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_{α}) = 10.53 cm^{-1}.

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 $3.0 < \theta < 25°$ 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 $I > 2.5\sigma(I)$, 319 reflections were retained. Lorentz and polarisation corrections were applied, but no corrections were made for absorption. The structure was solved by Patterson and Fourier techniques, and refined by full-matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms. The positions of the hydrogen atoms were calculated geometrically, and floated on the associated carbon atom, assuming C–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 0.005 with a refined weighting scheme, $w = k/[\sigma(F_o) + g(F_o)^2]$ and the final values of k and g were 6.0769 and 1.257×10^{-3}, respectively. Complex atom scattering factors [6] were employed and the Cu, Cl, and P atoms were corrected for anomalous dispersion. The final R value was 0.0487 and the maximum residual electron density was 0.35 e Å^{-3}. All calculations were carried out using the SHELX 76 [7] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and PUBTAB (K. Henrick) systems of programs on IBM 4341 and VAX 11/780 computers. The final atomic co-ordinates are given in Table 1, bond distances in Table 2, and bond angles in Table 3.

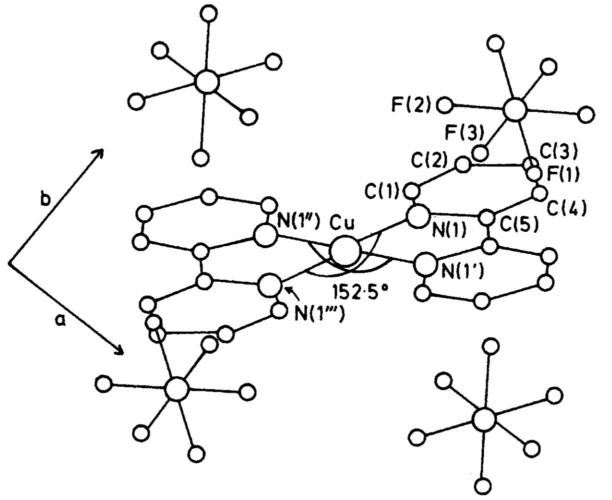

Figure 1. Molecular structure of $[Cu(bipy)_2][PF_6]_2$ viewed down the *c* axis showing the atom numbering scheme used

Figure 1 illustrates the molecular structure of (1), the atom numbering scheme used, and the crystal packing viewed down the *c* axis.

Electronic Properties.—Spectra were recorded as previously reported.[5,8] Figure 2(*a*) shows the polycrystalline e.s.r. spec-

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† *Supplementary data available* (No. SUP 23797, 5 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*
Cu	0.000 00	0.250 00	0.125 00
P	0.056 00(26)	0.000 00	0.250 00
F(1)	0.123 5(5)	0.047 0(6)	0.292 6(5)
F(2)	−0.012 2(5)	0.047 4(6)	0.291 7(4)
F(3)	0.054 6(6)	−0.065 9(5)	0.311 0(6)
N(1)	−0.043 6(5)	0.165 8(5)	0.061 1(8)
C(1)	−0.015 4(7)	0.148 7(7)	−0.002 7(12)
C(2)	−0.048 0(8)	0.087 0(8)	−0.045 0(8)
C(3)	−0.111 3(9)	0.039 6(7)	−0.018 7(10)
C(4)	−0.140 4(7)	0.057 1(6)	0.048 7(10)
C(5)	−0.105 6(6)	0.120 3(6)	0.089 8(5)

Table 2. Bond lengths (Å)

Cu−N(1)	1.985(11)	P−F(1)	1.561(7)
P−F(2)	1.562(7)	P−F(3)	1.576(9)
N(1)−C(1)	1.323(18)	N(1)−C(5)	1.362(12)
C(1)−C(2)	1.388(19)	C(2)−C(3)	1.378(17)
C(3)−C(4)	1.391(15)	C(4)−C(5)	1.405(14)
C(5)−C(5′)	1.445(15)		

Table 3. Bond angles (°)

F(2)−P−F(1)	89.7(5)	F(3)−P−F(1)	87.9(5)
F(3)−P−F(2)	87.3(5)	F(1)−P−F(1′)	90.8(7)
F(2)−P−F(2′)	89.8(8)	F(3)−P−F(3′)	178.4(5)
C(1)−N(1)−Cu	125.9(9)	C(5)−N(1)−Cu	113.5(1.0)
C(5)−N(1)−C(1)	120.4(1.1)	N(1)−Cu−N(1″)	103.6(8)
N(1)−Cu−N(1′)	83.0(7)	C(2)−C(1)−N(1)	123.2(1.4)
C(3)−C(2)−C(1)	118.9(1.0)	C(4)−C(3)−C(2)	118.1(1.3)
C(5)−C(4)−C(3)	121.5(1.2)	C(4)−C(5)−N(1)	118.1(1.1)

Table 4. Some relevant mean plane data (root-mean-square deviations in Å) for $[Cu(bipy)_2][PF_6]_2$, with deviations (Å) of atoms from planes in square brackets

	R.m.s.d.
Plane 1: N(1), C(1)—C(5)	0.0069
Plane 2: N(1′), C(1′)—C(5′)	0.0069
Plane 3: N(1), C(1)—C(5), N(1′), C(1′)—C(5′)	0.0146
Plane 4: N(1), N(1′), N(1″), N(1‴) [N(1) 0.4659, N(1′) −0.4659]	0.4659

Dihedral angles (°) between the mean planes: 1-2, 1.43°; plane 3 and symmetry related bipy mean plane, 44.6°.

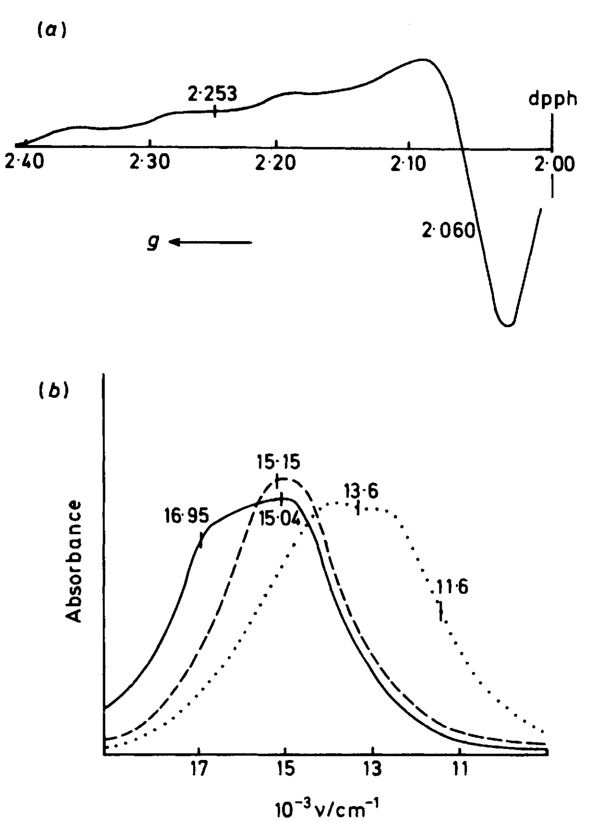


Figure 2. (*a*) Polycrystalline e.s.r. spectrum of $[Cu(bipy)_2][PF_6]_2$ at room temperature. (*b*) Electronic reflectance spectra of $[Cu(bipy)_2][PF_6]_2$ (——), $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$ (— — —), and $[Cu(bipy)_2(O_2NO)][NO_3]{\cdot}H_2O$ (· · · ·) (dpph = diphenylpicrylhydrazyl)

trum of (1), which is axial[5] with $g_{\parallel} = 2.253$ and $g_{\perp} = 2.060$ with clear evidence for copper hyperfine interactions on the high *g* value with $A_{\parallel} = 1.757 \times 10^{-2}$ cm^{-1}. Figure 2(*b*) shows the electronic reflectance spectrum of (1) which involves a broad band at 15 040 cm^{-1} with a clear high-energy shoulder at 16 950 cm^{-1}.

Results and Discussion

Crystal Structure.—The crystal structure of (1) comprises $[Cu(bipy)_2]^{2+}$ cations and $[PF_6]^-$ anions. The structure of the cation involves a four-co-ordinate CuN_4 chromophore, with a compressed tetrahedral geometry, with a dihedral angle of 44.6° (Table 4), and the copper atom occupying a special position of 222 symmetry.[9] The Cu−N distances are equivalent, 1.985 Å, with a N(1)−Cu−N(1‴) angle of 152.5°, and the bipy ligands bond symmetrically. There are no unusual bond lengths or angles in the bipy ligands,[10] the pyridine rings are near planar (r.m.s.d. = 0.0069 Å), and involve a relatively low[11] angle of twist (1.43°). The hexafluorophosphate ions involve a near regular octahedral co-ordination,[12] with the P atom on a two-fold special position; the mean P−F distance is 1.570 Å, and the mean F−P−F angle is 88.3°, with only limited evidence of disorder of the fluorine atoms.[13] The PF_6^- anions occupy positions relative to the CuN_4 chromophore, such that four long Cu−F distances (3.3 Å) are present to yield a distorted eight-co-ordinate CuN_4F_4 dodecahedral chromophore, but as the Cu−F distances are too long, even for semi-co-ordination[14] (*ca.* 2.4 Å), the copper stereochemistry is best considered as compressed tetrahedral.

The most interesting feature of the stereochemistry of (1) is that it involves a compressed tetrahedral four-co-ordinate CuN_4 chromophore, which is unique in the 34 $[Cu(bipy)_2X]Y$ type complexes of known crystal structure,[1–4] which to date have all been five- or six-co-ordinate. That the stereochemistry is compressed tetrahedral rather than rhombic coplanar is understandable as the bipy ligands cannot lie coplanar for steric reasons.[15] The tetrahedral CuN_4 conformation does arise, but only in chromophores with co-ordination numbers of five or six. It involves a near regular distortion in the elongated rhombic octahedral CuN_4X chromophore of $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$ (2) (dihedral angle 46.6),[16,17] $[Cu(bipy)_2(S_3O_6)]$,[18] $[Cu(bipy)_2(S_4O_6)]$ (56.3°),[19] and $[Cu(bipy)_2(F_2BF_2)][BF_4]$ (44.5°),[17] and in the bicapped CuN_4O_2 chromophores of $[Cu(bipy)_2(O_2NO)][NO_3]$ (3) (44.6°)[3,20] and $[Cu(bipy)_2(O_2S_2O_6)]$ (48.4°),[21] and a less regular distortion in the CuN_4O chromophore of $[Cu(bipy)_2(OH_2)][S_2O_6]$ (4).[4] This tetrahedral distortion of the CuN_4 chromophore contrasts with the much more frequent occurrence of a trigonal distortion of the $[Cu(bipy)_2]^{2+}$ cation in the $[Cu(bipy)_2X]Y$ com-

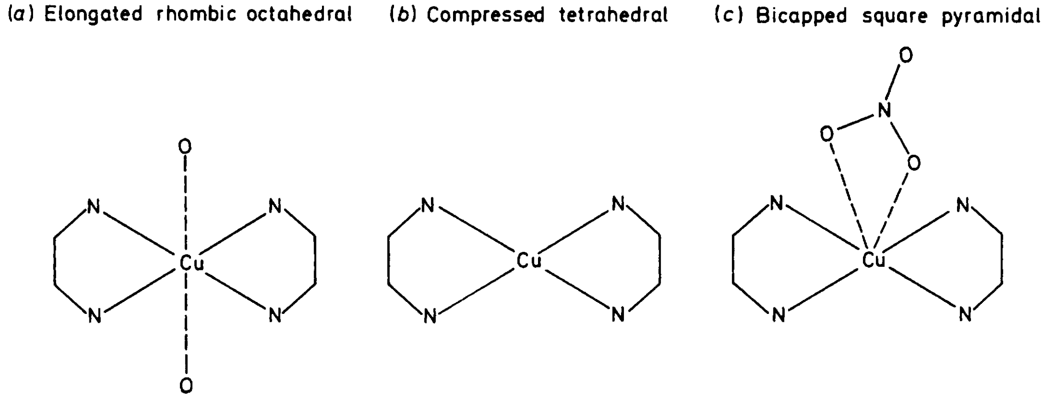


Figure 3. Molecular structures of (*a*) $[Cu(bipy)_2(O_2ClO_2)][ClO_4]$, (*b*) $[Cu(bipy)_2][PF_6]_2$, and (*c*) $[Cu(bipy)_2(O_2NO)][NO_3]\cdot H_2O$

plexes [1] (see ref. 21 for an earlier discussion). It is equally clear that the $[Cu(bipy)]^{2+}$ cation readily increases its co-ordination number above four by co-ordination or semi-co-ordination [14] of even weakly co-ordinating polyanions such as the NO_3^-,[20] ClO_4^-,[19] and BF_4^- [19] ions. As PF_6^- is equally well established as a co-ordinating [22] polyanion and is also known to be involved in semi-co-ordination,[23] to the copper(II) ion in $[CuL(OH_2)(PF_6)][PF_6]$ (L = 5,7-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,7-diene and $[Cu(en)_2(OH_2)(PF_6)][PF_6]$ (en = ethylenediamine),[23] it is not apparent why the $[PF_6]^-$ anions of (1) are not involved in even semi-co-ordination to the copper(II) ion to give a rhombic octahedral CuN_4F_2 chromophore as occurs in $[Cu(bipy)_2(F_2BF_2)][BF_4]$.[17]

Although the tetrahedral CuN_4 chromophore has not yet been recognised in the [Cu(phen)$_2$X]Y series of complexes, where phen is the rigidly planar 1,10-phenanthroline ligand, it does occur in $[Cu(bipyam)_2][ClO_4]_2$ (5),[24] where bipyam is the more flexible di-2-pyridylamine ligand, with a dihedral angle of 55.6°, compared to that of 44.6° in (1).

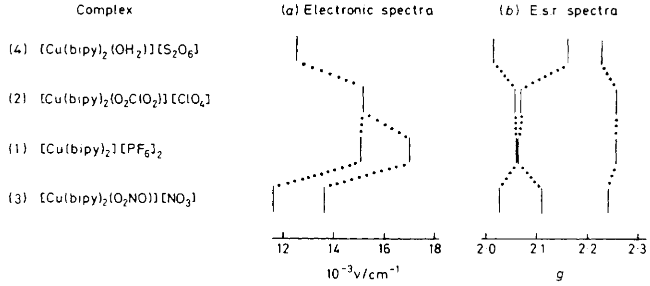
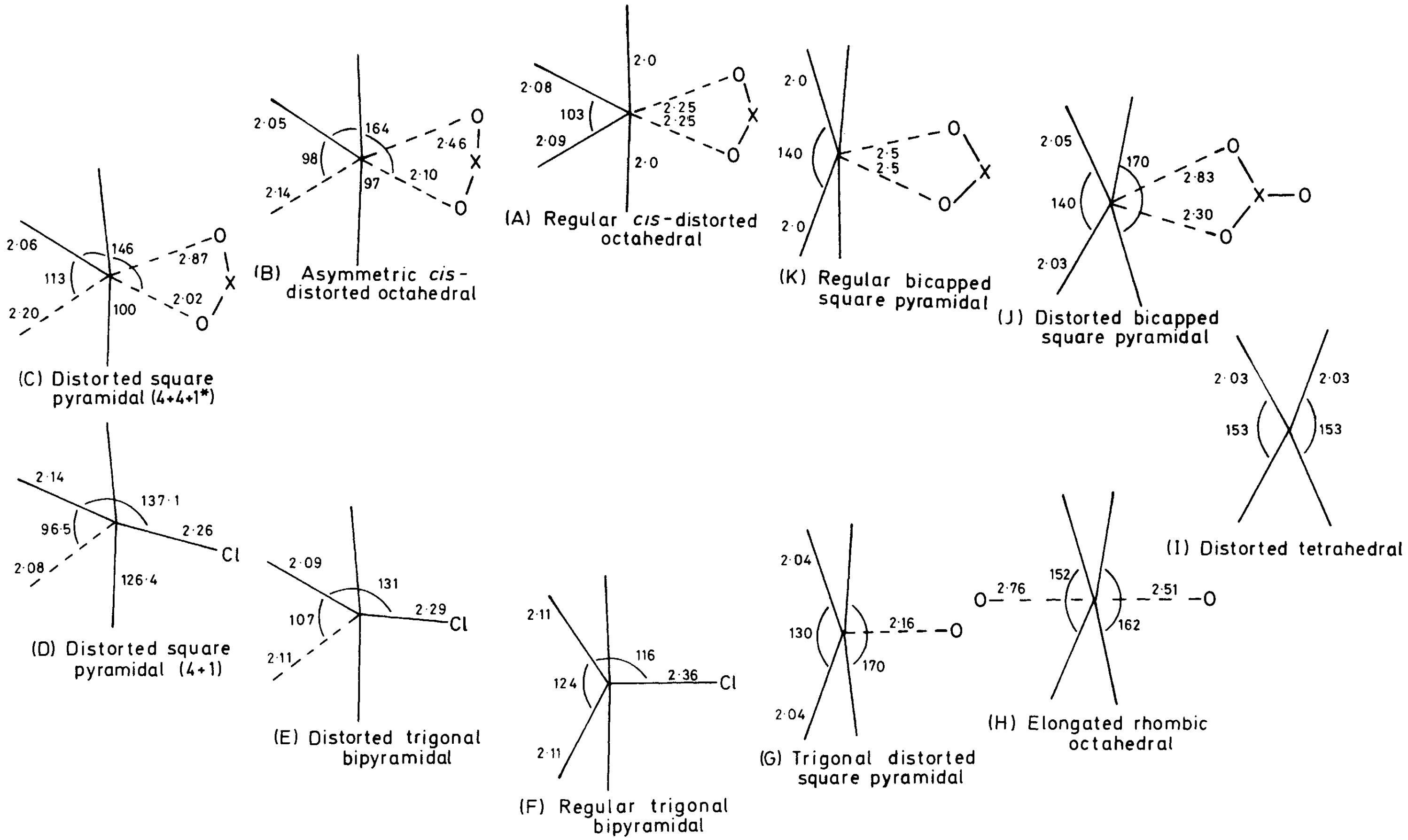


Figure 4. Electronic properties of some [Cu(bipy)$_2$X]Y complexes

Electronic Properties.—The axial e.s.r. spectrum of (1) is consistent [5] with the compressed tetrahedral stereochemistry of the CuN_4 chromophore and a $d_{x^2-y^2}$ (or d_{xy}) ground state ($g_\parallel \gg g_\perp > 2.0$). A combination of the observed copper hyperfine coupling, serious misalignment [5] ($2\gamma = 90°$), and a poorly defined morphology made it impractical to record accurate single-crystal data. Nevertheless, the approximate single-crystal *g* values, 2.245, 2.058, and 2.047 have a small rhombic component and are only consistent with a $d_{x^2-y^2}$ ground state for the CuN_4 chromophore of (1), a ground state which is consistent with that previously observed [25] in (5). The electronic reflectance spectrum shows a broad band at 15 040 cm^{-1} with a clear high-energy shoulder at 16 950 cm^{-1}. As there is no evidence for a low-energy shoulder, all four *d-d* transitions in the copper(II) ion must lie within this band envelope, in the range 14 000—18 000 cm^{-1}. The high-energy shoulder at 16 950 cm^{-1} is the highest-energy band observed in the complexes [Cu(bipy)$_2$X]Y [1-4,16-21,26] and offers an ' electronic criterion of stereochemistry ',[27] to distinguish the compressed tetrahedral CuN_4 chromophore from adjacent stereochemistries. These are the elongated rhombic octahedral [16] CuN_4O_2 as in (2), Figure 3(*a*), and the bicapped square-pyramidal chromophore [20] of (3), Figure 3(*c*), whose electronic reflectance spectra are included in Figure 2(*b*). All three complexes, (1)—(3), involve an approximate $d_{x^2-y^2}$ ground state, defined by their e.s.r. spectra and enable these stereochemistries to be distinguished from that of the trigonal distorted square-pyramidal CuN_4O chromophore [4] of (4). The latter is characterised by a single-peaked electronic spectrum (12 450 cm^{-1}) and rhombic *g* values, $g_3 = 2.225$, $g_2 = 2.158$, and $g_1 = 2.011$, which are consistent with an approximate d_{z^2} ground state ($g_3 \approx g_2 > g_1 \approx 2.0$). The electronic properties of (1)—(4) are summarised in Figure 4 and together offer a convenient ' electronic criterion of stereochemistry ' for these four stereochemistries of the [Cu(bipy)$_2$X]Y series of complexes. This criterion then establishes for the [Cu(bipy)$_2$X]Y complexes a structural pathway,[28] Figure 5, connecting the regular *cis*-distorted octahedral [2] and regular trigonal bipyramidal [1] stereochemistries, the left-hand side of which, (A)—(F), has been previously established for the distorted [Cu(bipy)$_2$(ONO)]X [2] and [Cu(bipy)$_2$Cl]Y [1] complexes. This structural pathway for the [Cu(bipy)$_2$X]Y complexes then represents not only a convenient summary of the sense of distortions present connected by a linear combination of the appropriate normal modes of vibration, but also the variation of the e.s.r. and electronic spectra in this series of complexes, Figure 4.

Assignment of the Electronic Spectrum.—Owing to two-dimensional misalignment of the local molecular axes of (1) and an unfavourable morphology, it was not possible to determine the polarised single-crystal spectrum for (1). Nevertheless, the electronic reflectance spectra suggested that all four possible transitions lie within the range 14 000—18 000 cm^{-1}, that is at significantly higher energy than the three bands observed [25] in (5) at 10 400, 13 500, and 15 700 cm^{-1}. The higher energy for (1) is consistent with the significantly lower dihedral angle of 44.6° compared with that of 55.6° in (5). An earlier attempt to assign the polarised single-crystal spectrum [25] of (5) was unsatisfactory for a number of reasons: firstly, the ambiguity between the *g* value directions and those of the polarised spectra and although the cause of this phenomenon is understandable,[29] it does not remove the ambi-



(A) Regular *cis*-distorted octahedral

(B) Asymmetric *cis*-distorted octahedral

(C) Distorted square pyramidal (4+4+1*)

(D) Distorted square pyramidal (4+1)

(E) Distorted trigonal bipyramidal

(F) Regular trigonal bipyramidal

(G) Trigonal distorted square pyramidal

(H) Elongated rhombic octahedral

(I) Distorted tetrahedral

(J) Distorted bicapped square pyramidal

(K) Regular bicapped square pyramidal

Figure 5. Structural pathway for some [Cu(bipy)$_2$X]Y complexes: bond lengths (Å) and angles (°)

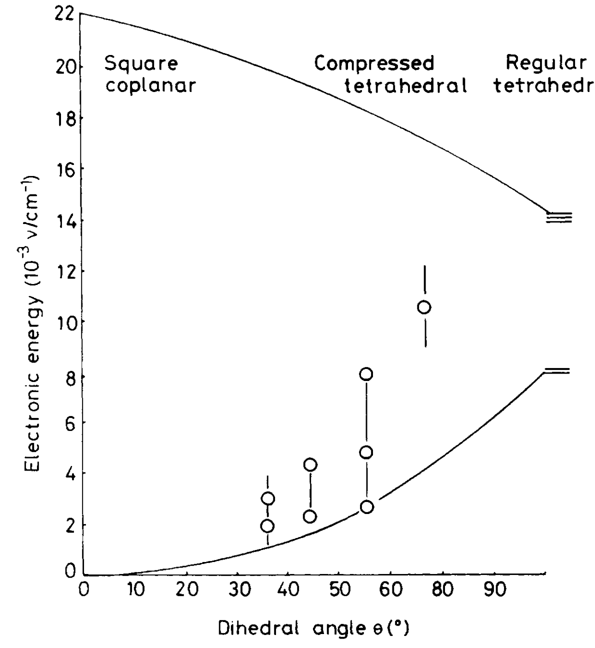


Figure 6. Variation of the electronic energies of some compressed tetrahedral CuN$_4$ complexes as a function of the dihedral angle, θ (see text for reasons for limited assignments): band positions (O), and spread of energy levels (vertical lines)

guity; secondly, the inclusion of a band at 18 700 cm^{-1} as *d–d* in origin, which is now considered to be a ligand charge-transfer band; and thirdly, the uncertainty in the appropriate effective electronic symmetry to be used. The polarised single-crystal spectra do indicate three bands which are clearly lower in energy than those in (1), but the situation is further complicated by the report [30] of a weak band at 7 500 cm^{-1} in the electronic reflectance spectrum of (5), the evidence for which we find most unconvincing. Nevertheless, an attempt has been made [30] to assign the one-electron energy levels of a number of complexes containing compressed tetrahedral CuN$_4$ chromophores as a function of the dihedral angle [see Figure 3 of ref. 30*b*]. While this attempt is commendable,[30] the range of dihedral angles was restricted to 53.8—58.8°, and included the questionable band at 7 500 cm^{-1} in (5). The attraction of (1) is that it provides an example of a compressed tetrahedral CuN$_4$ chromophore with a dihedral angle significantly different from that of (5), namely, 44.6°, and offers a better possibility of establishing a dihedral angle *versus* electronic energy correlation. If the range of electronic energies reported for two further copper(II) complexes containing compressed tetrahedral chromophores with significantly different dihedral angles of 37 and 67° are included [31,32] the results of Figures 5 and 6 are obtained. A reasonable correlation of the electronic energies is then obtained with the variation of the dihedral angle over a 30° range, but it is still not possible to suggest a convincing assignment of the one-electron orbital levels of (5) (but see Figure 12 of ref. 33).

Acknowledgements

The authors acknowledge the award of a senior demonstratorship (to S. T.), a senior studentship (to J. F.), and are grateful to Drs. P. G. Owston, M. McPartlin, and K. Henrick (Polytechnic of North London) for help in data collection, to Professor G. M. Sheldrick, Dr. S. Motherwell (Cambridge University), and Dr. K. Henrick (Polytechnic of North London), for the use of their programs.

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Received 11*th March* 1983; *Paper* 3/387