Crystal Structure † of Bis(2,2′-bipyridyl)monochlorocopper(II) Hexafluorophosphate Monohydrate at 298 K and the Electron Spin Resonance Spectra of some Bis(2,2′-bipyridyl)copper(II) Complexes to 4.2 K

Suresh Tyagi and Brian Hathaway *
The Chemistry Department, University College, Cork, Ireland
Stefan Kremer, Horst Stratemeier, and Dirk Reinen
The Chemistry Department, University of Marburg, Federal Republic of Germany

The crystal structure of the title compound $[Cu(bipy)_2Cl][PF_6]\cdot H_2O$ (1) (bipy = 2,2′-bipyridyl) has been determined by *X*-ray diffraction, using diffractometer data collection. The structure was solved by the heavy-atom method and successive Fourier synthesis. Compound (1) crystallises in the monoclinic space group $P2_1/n$ with $a = 21.403(5)$, $b = 12.235(3)$, $c = 8.599(2)$ Å, $\beta = 92.68(2)°$, and $Z = 4$. The CuN_4Cl chromophore involves a near-regular trigonal bipyramidal stereochemistry, but with a significant distortion of the three in-plane angles from 120° (115.7, 123.8, and 120.5°). The polycrystalline and single-crystal e.s.r. spectrum of (1) and a number of other 2,2′-bipyridyl complexes with $[Cu(bipy)_2X]^{n+}$ cations [X = Cl or I, $n = 1$; X = NH_3, $n = 2$) are reported between 300 and 4 K. The molecular *g* tensors are consistent with a near-regular trigonal bipyramidal or square pyramidal distorted trigonal bipyramidal stereochemistry. As the e.s.r. spectra do not change significantly with temperature a dynamic behaviour in the sense of the pseudo-rotation of the Berry–Twist mechanism is not considered to operate.

There is evidence that the reported compressed trigonal bipyramidal geometry of the $[CuCl_5]^{3-}$ anion in the compounds $[M^{III}(NH_3)_6][CuCl_5]$ (M^{III} = Cr or Co)[1,2] at 298 K is the dynamic average over three elongated square pyramidal conformations,[3] which can be frozen out at low temperature. In line with this model, structural and spectroscopic results on $Cu^{II}L_5$ polyhedra with L = Cl or Br or a N or O donor are generally in accord with a square pyramidal stereochemistry which is elongated in the apical directions.[4] A compressed trigonal bipyramid may eventually be stabilized, if geometric ligand effects (polydentate ligands) and/or packing effects (bridging ligands) are present.[3] In order to determine whether a fluxional behaviour of the above kind also applies to the near-regular trigonal bipyramidal stereochemistry of the copper(II) ion involving two bidentate 2,2′-bipyridyl (bipy) ligands and a fifth non-equivalent ligand the crystal structure of $[Cu(bipy)_2Cl][PF_6]\cdot H_2O$ (1) has been determined. The e.s.r. spectra of this complex and of a number of comparable near-trigonal bipyramidal copper(II) complexes have been measured to 4.2 K and are now also reported.

Experimental

Preparation.—$CuCl_2\cdot 2H_2O$ (0.737 g, 0.8 mmol) and bipy (0.25 g, 1.6 mmol) were dissolved in water–ethanol (1 : 1, 30 cm³), the solution was warmed, stirred, and KPF_6 (0.147 g, 0.8 mmol) added. The blue solution was filtered and left to evaporate in air. After 3—4 d small well formed blue crystals of (1) were deposited (Found: C, 41.5; H, 3.15; Cl, 6.20; Cu, 11.20; N, 9.70. $C_{20}H_{18}ClCuF_6N_4OP$ requires C, 41.80; H, 3.15; Cl, 6.70; Cu, 11.05; N, 9.75%). The complexes $[Cu(bipy)_2Cl]Cl\cdot 6H_2O$ (2) and $[Cu(bipy)_2(NH_3)][BF_4]_2$ (3) were prepared as previously described.[4–9]

Crystal Data for $[Cu(bipy)_2Cl][PF_6]\cdot H_2O$ (1).—$C_{20}H_{18}ClCuF_6N_4OP$, $M = 573.97$, monoclinic, space group $P2_1/n$, $a = 21.403(5)$, $b = 12.235(3)$, $c = 8.599(2)$ Å, $\beta = 92.68(2)°$, $U = 2\,249.32$ Å³, $D_m = 1.63(2)$, $Z = 4$, $D_c = 1.69$ g cm⁻³, $F(000) = 1\,156$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, and $\mu(\text{Mo-}K_\alpha) = 11.75$ cm⁻¹. The unit-cell parameters were determined, the intensities collected (2 094 reflections were retained), the structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares analysis, as described previously.[10] 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 final values of *k* and *g* of 1.288 and 1.096×10^{-3}, respectively. The final *R* value was 0.0521 and the maximum residual electron density was 0.347 e Å⁻³. All calculations were carried out by using SHELX 76[11] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and PUBTAB (K. Henrick) systems of programs on the IBM 4341 and VAX 11/780 computers. The final atomic co-ordinates are given in Table 1, and selected bond lengths and angles in Table 2. Figure 1 illustrates the molecular structure of (1), the atom-numbering scheme used, and the crystal packing. Figure 2 illustrates the local molecular structures of complexes (1)—(5).

Spectroscopic Measurements.—E.s.r. spectra were recorded on an E15 Varian spectrometer (*Q*- and *X*-band) at 298, 77, and 4.2 K, with diphenylpicrylhydrazyl (dpph) as internal standard ($g = 2.003_7$). The electronic reflectance spectra were recorded by a Zeiss PMQ II spectrophotometer (Infrasil) with a low-temperature attachment. Sr_2ZnTeO_6 (4 000—12 000 cm⁻¹) and freshly sintered MgO (8 000—30 000 cm⁻¹) were used as standards.

Results and Discussion

Crystal Structure.—The crystal structure of (1) consists of a $[Cu(bipy)_2Cl]^+$ cation, a $[PF_6]^-$ anion, and a molecule of non-bonded water. The structure of the cation involves a five-co-ordinate CuN_4Cl chromophore with an almost regular trigonal bipyramidal stereochemistry,[9] with no evidence for

---

† *Supplementary data available* (No. SUP 23984, 24 pp.): all thermal parameters, H-atom co-ordinates, full bond lengths and angles, least-squares planes, non-bonded distances, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional atomic co-ordinates for $[Cu(bipy)_2Cl][PF_6]\cdot H_2O$ (1)

Atom	x	y	z
Cu	−0.029 27(4)	0.747 80(8)	0.772 94(10)
Cl	0.017 4(1)	0.853 3(2)	0.582 6(2)
N(1)	−0.095 5(3)	0.693 8(5)	0.621 0(7)
C(1)	−0.137 0(4)	0.760 4(7)	0.543 3(9)
C(2)	−0.183 1(4)	0.720 5(7)	0.442 6(10)
C(3)	−0.187 0(4)	0.610 5(8)	0.419 0(9)
C(4)	−0.144 8(4)	0.540 8(7)	0.496 1(9)
C(5)	−0.098 3(3)	0.585 8(6)	0.595 3(8)
C(6)	−0.047 8(3)	0.522 4(6)	0.674 9(8)
C(7)	−0.039 3(4)	0.410 2(6)	0.647 9(9)
C(8)	0.012 5(4)	0.359 7(6)	0.717 9(9)
C(9)	0.052 3(4)	0.416 5(6)	0.819 9(9)
C(10)	0.040 6(4)	0.5272(6)	0.844 8(8)
N(2)	−0.008 0(3)	0.579 8(4)	0.771 3(6)
N(3)	0.032 9(3)	0.798 6(5)	0.939 1(7)
C(11)	0.094 8(3)	0.781 5(6)	0.936 8(9)
C(12)	0.135 3(4)	0.818 5(7)	1.056 0(10)
C(13)	0.111 9(4)	0.881 7(7)	1.172 6(9)
C(14)	0.048 6(4)	0.902 8(6)	1.177 2(9)
C(15)	0.010 0(3)	0.857 7(5)	1.056 1(8)
C(16)	−0.059 5(3)	0.869 8(5)	1.052 3(7)
C(17)	−0.091 5(4)	0.922 5(6)	1.166 4(9)
C(18)	−0.155 7(4)	0.927 9(7)	1.152 0(10)
C(19)	−0.187 6(4)	0.878 8(7)	1.026 4(11)
C(20)	−0.152 9(4)	0.825 7(6)	0.917 8(9)
N(4)	−0.090 4(3)	0.820 3(4)	0.928 3(6)
P	0.275 4(1)	−0.009 1(2)	0.436 9(2)
F(1)	0.268 9(4)	0.093 8(5)	0.329 5(8)
F(2)	0.292 6(3)	0.066 6(4)	0.585 4(6)
F(3)	0.347 1(2)	−0.020 0(6)	0.404 5(6)
F(4)	0.258 5(2)	−0.086 9(5)	0.292 1(6)
F(5)	0.280 9(3)	−0.113 6(4)	0.547 8(7)
F(6)	0.202 9(2)	0.000 2(5)	0.472 0(7)
O	0.343 5(4)	0.247 6(6)	0.924 5(9)

Table 2. Selected bond lengths (Å) and bond angles (°) for $[Cu(bipy)_2Cl][PF_6]\cdot H_2O$ (1)

Cu–Cl	2.344(2)	Cu–N(1)	1.996(6)
Cu–N(2)	2.105(6)	Cu–N(3)	2.005(6)
Cu–N(4)	2.108(6)	N(1)–C(1)	1.358(9)
P–F(2)	1.606(5)	P–F(1)	1.564(6)
P–F(4)	1.595(5)	P–F(3)	1.578(5)
P–F(6)	1.599(5)	P–F(5)	1.596(6)
N(1)–Cu–Cl	92.2(2)	N(2)–Cu–Cl	115.7(2)
N(2)–Cu–N(1)	79.6(2)	N(3)–Cu–Cl	92.1(2)
N(3)–Cu–N(1)	175.5(2)	N(3)–Cu–N(2)	99.8(2)
N(4)–Cu–Cl	120.5(2)	N(4)–Cu–N(1)	96.4(2)
N(4)–Cu–N(2)	123.8(2)	N(4)–Cu–N(3)	80.1(2)
F(2)–P–F(1)	90.9(4)	F(3)–P–F(1)	91.4(4)
F(3)–P–F(2)	90.0(3)	F(4)–P–F(1)	90.5(4)
F(4)–P–F(2)	178.6(4)	F(4)–P–F(3)	89.9(3)
F(5)–P–F(1)	179.0(4)	F(5)–P–F(2)	88.8(3)
F(5)–P–F(3)	89.6(4)	F(5)–P–F(4)	89.8(3)
F(6)–P–F(1)	89.7(4)	F(6)–P–F(2)	89.9(3)
F(6)–P–F(3)	179.0(4)	F(6)–P–F(4)	90.2(3)
F(6)–P–F(5)	89.4(4)		

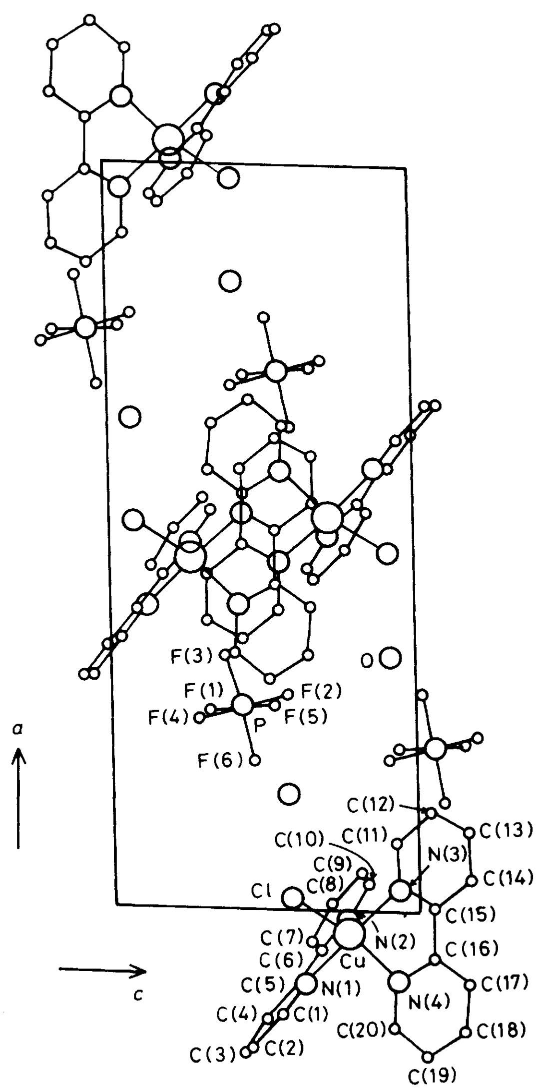

Figure 1. Molecular structure of $[Cu(bipy)_2Cl][PF_6]\cdot H_2O$ (1) the atom-numbering scheme used, and the crystal packing

even semi-co-ordination [12] of either the $[PF_6]^-$ anion or of the lattice water. Although the $[PF_6]^-$ anion occupies a general position, it involves a near-regular octahedral structure,[13] mean P–F distance, 1.59 Å, and a mean F–P–F angle, 89.8°, with no evidence for the disorder [14] normally associated with this anion. There are no unusual bond lengths or angles in the bipy ligands,[15] the individual pyridine rings are reasonably planar (see SUP No. 23984), and within each bipy ligand the pyridine rings are twisted with respect to each other by 9.07 and 4.17°, respectively, within the range of 0—13° previously observed for the angle of twist of the bipy ligand.[16] The mean planes of the bipy ligands make an angle of 127° to each other. Within the CuN_4Cl chromophore the axial Cu–N distances, mean 2.00 Å, are not significantly different, and *ca.* 0.1 Å shorter than the two equatorial Cu–N distances (mean 2.11 Å), as has been found previously for the trigonal bipyramidal stereochemistry.[17] In the CuN_4Cl chromophore of (1), the out-of-plane angles are 90 ± 10°, and the N(1)–Cu–N(3) angle is nearly linear, at 175.5°. In the Cu,N(2),N(4),Cl plane, the angles are near trigonal, but with the N(2)–Cu–N(4) (α_3) angle greater than 120° (123.8°) and the Cl–Cu–N(2) (α_1) angle less than 120° (115.7°). In general, the structure of (1), Figure 2(*a*), is comparable to that previously observed [18–21] for the $[Cu(bipy)_2Cl]^+$ cation in a series of five complexes; it is closest to that of complex (2) [Figure 2(*b*)] and significantly different from the square pyramidal distorted structure [21] of $[Cu(bipy)_2Cl][ClO_4]$. The most significant differences in complexes (1) and (2) are in the angles α_1, α_2, and α_3, Figure 2(*a*), with $\alpha_3 - \alpha_1 = 8°$, a difference that is difficult to explain if the structure of (1) lies on the structural pathway (ref. 19,

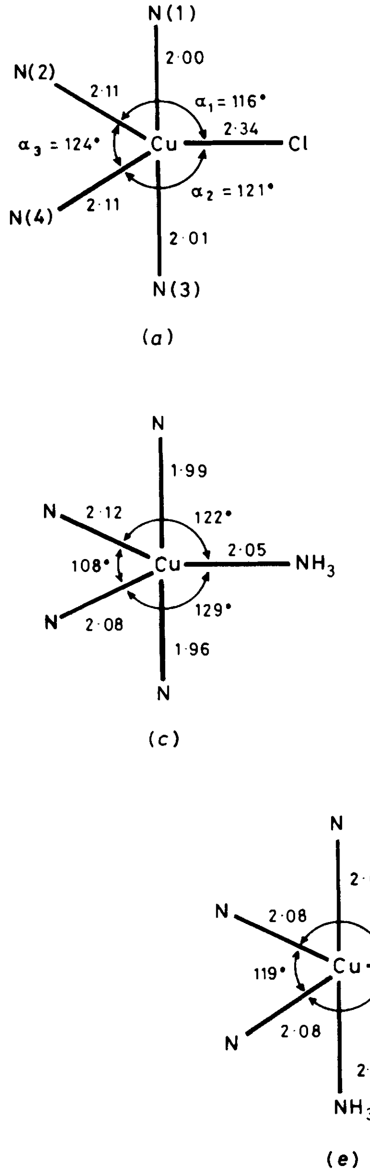

Figure 2. Molecular structures of (*a*) [Cu(bipy)Cl][PF$_6$]·H$_2$O (1); (*b*) [Cu(bipy)$_2$Cl]Cl·6H$_2$O (2); (*c*) [Cu(bipy)$_2$(NH$_3$)][BF$_4$]$_2$ (3); (*d*) [Cu(bipy)$_2$I]I (4); and (*e*) [Cu(tren)(NH$_3$)][ClO$_4$]$_2$ (5)

Figure 4), previously suggested to correlate the structures of five cation distortion isomers[22] of the [Cu(bipy)$_2$Cl]$^+$ cation. Thus, although the structure of (1) has been slightly more accurately determined than (2), its structure does not fit quite so neatly on the above structural pathway,[19] however its structure is closer to that of (2) rather than that of [Cu(bipy)$_2$Cl][ClO$_4$].[21]

Electronic Properties.—The unit cell of (1) contains CuN$_4$Cl polyhedra with two different orientations of the trigonal axes, which are misaligned[23] by $2\alpha \simeq 37°$ with respect to one another. The single-crystal e.s.r. spectrum (*Q*-band) yields two independent signals of equal intensity, indicating that no exchange-narrowing occurs, in agreement with the very long Cu–Cu distances (>11 Å) between the symmetry related chromophores. Hence the observed crystal *g* tensor equates with the local molecular *g* values [$g_z = 2.00_4$, $g_y = 2.17_5$, and $g_x = 2.19_3$ (298 K, single-crystal and powder values)]. It is consistent with the near-regular trigonal bipyramidal structure [Figure 2(*a*)],[23] which implies a d_{z^2} ground state for a regular D_{3h} symmetry and *g* values[24] (second-order contributions only) according to equation (i).

$$g_\parallel = g_0;\quad g_\perp = g_0 + 6u_\perp;\quad u_\perp = \frac{k_\perp{}^2\lambda_0}{E(A_2'\rightarrow E'')} \qquad \text{(i)}$$

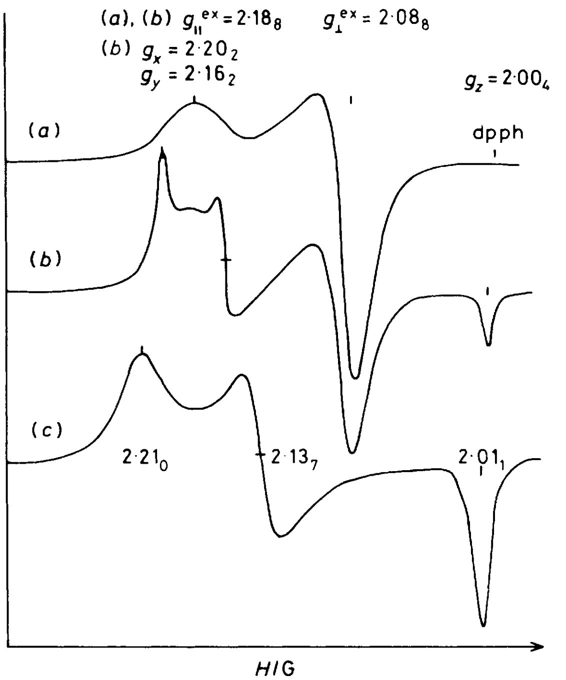

Figure 3. E.s.r. powder spectra (*Q*-band frequency, 298 K) of [Cu(bipy)$_2$Cl]Cl·6H$_2$O (2) [(*a*) and (*b*) different crystallisation procedures] and (*c*) [Cu(bipy)$_2$(NH$_3$)][BF$_4$]$_2$ (3)

The *g* tensor does not change down to 4 K, indicating a non-fluxional geometry for the CuN$_4$Cl polyhedra.[25] g_z is connected with the axial Cu–N(1,3) direction, while g_y has an orientation not too far from the equatorial Cu–Cl direction. The electronic reflectance spectrum at 298 K shows a broad unresolved band at *ca.* 12 000 cm^{-1} and an asymmetry around 15 000 cm^{-1}, which may be tentatively assigned to the $A'\rightarrow E'$ and E'' transitions in an approximate D_{3h} symmetry. With these energies and an orbital contribution, $u_\perp$, of 0.03 a covalency parameter $k_\perp \simeq 0.75$ * can be estimated [equation (*i*)], in accord with comparable values for [Cu(terpy)Cl$_2$] (terpy = 2,2′ : 6′,2″-terpyridyl) complexes.[26] The e.s.r. spectrum of (1) is very similar to that of [Cu(NH$_3$)$_2$Ag(SCN)$_3$][27] with polyhedra of D_{3h} symmetry whose geometry is also non-fluxional with *g* values, $g_\parallel = 2.00_2$ and $g_\perp = 2.19_7$, between 298 and 4.2 K.

The complex [Cu(bipy)$_2$Cl]Cl·6H$_2$O (2) involves CuN$_4$Cl polyhedra[18] of almost the same geometry as those of complex (1) [Figure 2(*a*) and (*b*)]. Although the unit cell contains two spectroscopically different Cu^{2+} polyhedra,[18] only one signal is observed in the single-crystal e.s.r. experiment ($g_1^{ex} = 2.08_2$, $g_2^{ex} = 2.09_2$, and $g_3^{ex} = 2.18_7$). Hence the *g* tensor is exchange(ex) coupled, which is expected considering the short Cu–Cu spacing of 4.3 Å. The powder spectrum (298 or 100 K) is critically dependent on the velocity of crystallisation and the

---

* *k* is used as an empirical parameter, which additionally confirms the assignments of the ligand-field transitions by comparison with *k* values for Cu–N bonds in related compounds.

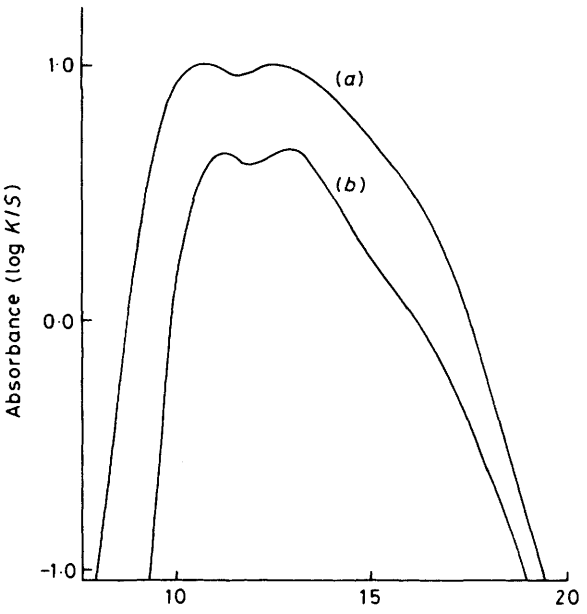

Figure 4. Electronic powder reflectance spectra (5 K) of (*a*) [Cu(bipy)$_2$Cl]Cl·6H$_2$O (2) and (*b*) [Cu(bipy)$_2$(NH$_3$)][BF$_4$]$_2$ (3)

grinding procedure used. Besides broad signals, which imply the single-crystal *g* values, a second *g* tensor with the components $g_z = 2.00_4$, $g_y = 2.16_2$, and $g_x = 2.20_2$ is clearly visible (Figure 3). Because the additional *g* tensor is very similar to the one observed for (1), the e.s.r. powder spectrum of (2) appears to exhibit the molecular and co-operative *g* tensors side by side. Assuming axial molecular *g* tensors for the two CuN$_4$Cl polyhedra and misalignment angles with respect to one another of 90° ['antiferrodistortive order'],[24] the exchange-narrowed *g* tensor of equations (ii) is expected in

$$g_{\parallel}^{\mathrm{ex}} = g_{\perp} = g_0 + 6u_{\perp};$$
$$g_{\perp}^{\mathrm{ex}} = \tfrac{1}{2}(g_{\parallel} + g_{\perp}) = g_0 + 3u_{\perp} \qquad \text{(ii)}$$

approximate agreement with the molecular and co-operative *g* values of Figure 3(*a*) and (*b*). Actually the molecular *g* tensors are orthorhombic and the canting angles between them deviate from 90°. We have calculated the orientations of the molecular *g*-tensor components with respect to the Cu^{2+}–ligand directions utilising the general equations given by Chao,[28] which correlate the molecular with the exchange-coupled *g* values. We find that the smallest molecular *g* value (2.00_4) is connected with the (pseudo) trigonal N(1)–Cu–N(3) axis within 6°, while the largest *g* component (2.20_2) deviates only *ca.* 3° from the Cu–N(4) direction [Figure 2(*b*)]. The e.s.r. powder spectrum does not change down to 4.2 K. Obviously the trigonal bipyramidal geometry of the CuN$_4$Cl chromophore in (2) is also non-fluxional. The ligand-field spectrum at 298 K is similar to the spectrum of (1). At 5 K two peaks at 10 900 and 12 800 cm^{-1} are clearly resolved and a shoulder is indicated around 15 500 cm^{-1} (Figure 4). With an assignment of the maxima to the split-states of the trigonal bipyramidal $^2E'$ level and the broad shoulder to the $^2E''$ state, the same covalency parameter, $k_{\perp} \simeq 0.75$, as for compound (1) is obtained. A splitting in particular of the excited $^2E'$ state (connected with the in-plane σ- and π-antibonding $d_{x^2-y^2}$ and d_{xy} orbitals) is expected, because different ligands are present in the equatorial plane of the CuN$_4$Cl chromophore (non-axial *g* tensor). It is finally interesting to note that the *g* tensor of the [Cu(bipy)$_2$Cl]$^+$ cation in dilute frozen methanol solution ($g_z = 2.00_3$, $g_y = 2.16_7$, and $g_x = 2.19_0$) is very similar to those of (1) and (2). Obviously the stable geometry of the [Cu(bipy)$_2$Cl]$^+$ chromophore is trigonal bipyramidal. Deviations towards a square pyramid are thus presumably induced by packing effects [19] in the solid compounds.

In [Cu(bipy)$_2$(NH$_3$)][BF$_4$]$_2$ (3) the geometry of the CuN$_5$ chromophore [Figure 2(*c*)] deviates from trigonal bipyramidal towards square pyramidal [29] with one equatorial Cu–N bond length appreciably longer than the other two. This behaviour matches with the preference of Cu^{2+} in a ligand field of five equal unidentate ligands for an apically elongated square pyramid with respect to a compressed trigonal bipyramid.[3] The unit cell of (3) contains two pairs of Cu^{2+} polyhedra, connected by an inversion centre. The spacing between the Cu^{2+} ions of each pair is 8.1_5 Å which is still in the range where exchange interaction might occur.[26] In the single-crystal e.s.r. experiment [8] only one signal is observed with *g* values $\simeq 2.00_5$, $\simeq 2.13_5$, and $\simeq 2.20_5$. Because the crystallographic data [29] indicate that the canting angles between the molecular *g* tensors of the two Cu^{2+} sites are presumably very small, the experimental *g* values reflect the molecular CuN$_5$ geometry to a first approximation. The powder e.s.r. spectrum [2.01_1 (2.00_5), 2.13_7 (2.13_7), 2.21_0(2.20_9) at 298(77) K] (Figure 3) does not change significantly between 77 and 4.2 K and indicates again a non-fluxional geometry of the Cu^{2+} polyhedron. The ligand-field spectra are comparable to those of (2) (Figure 4). At 5 K two peaks at 11 450 and 13 200 cm^{-1} are resolved, and a further transition appears as a distinct shoulder around 15 500 cm^{-1}. The covalency parameter $k_{\perp} \simeq 0.74$ is again consistent with those of (1) and (2). The perchlorate salt, [Cu(bipy)$_2$(NH$_3$)][ClO$_4$]$_2$, is isostructural with (3), as the *X*-ray powder diagrams and e.s.r. spectra are nearly identical.

The e.s.r. powder spectrum [9] of [Cu(bipy)$_2$I]I is molecular, $g_{\perp} = 2.16_0$, $g_{\parallel} = 2.02_7$, in close agreement with reported single-crystal data,[9] and also does not change down to 4.2 K. The structural data indicate a slightly distorted trigonal bipyramid, Figure 2(*d*), although the standard deviations are rather large.[30] The strictly axial *g* tensor and the significant deviation of $g_{\parallel}$ from the spin-only value [equation (i)] are difficult to interpret, however.

The 2% copper(II)-doped [Zn(tren)(NH$_3$)][ClO$_4$]$_2$ [tren = tris(2-aminoethyl)amine] system has been reported [31] to have an electronic reflectance spectrum comparable to that of the concentrated copper complex (5), indicating that the CuN$_5$ stereochemistry, Figure 2(*e*), is the same in the concentrated and doped system.[32] The e.s.r. spectrum of the doped complex shows [31] copper hyperfine and *g* values consistent with a d_{z^2} ground state at 298, 77, and 4.2 K at *Q*-band frequency, *i.e.* $g_{\parallel} = 2.00_2$, $g_{\perp} = 2.16_8$. The spectrum also yields a weak signal at 2.08_7, which may be ascribed to the $g_{\perp}^{\mathrm{ex}}$ value of Cu^{2+}–Cu^{2+} pairs [equation (ii)], and shows no variation in form down to 4 K that would be consistent with a change in stereochemistry to square pyramidal.

Acknowledgements

The authors acknowledge the award of a Senior Demonstratorship (to S. T.), and are grateful to Drs. P. G. Owston, M. McPartlin, and K. Henrick (Polytechnic of North London) for help in data collection, to Drs. G. M. Sheldrick and S. Motherwell (Cambridge University) and K. Henrick (Polytechnique of North London), for the use of their programs, the Computer Bureau, U.C.C. for computing facilities, and the Microanalysis Section, U.C.C. for microanalysis.

References

1 K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1111.

2 I. Bernal, J. D. Korp, E. O. Schlemper, and M. S. Hussain, *Polyhedron*, 1982, **1**, 365; W. Massa, unpublished work.

3 D. Reinen, Jahn–Teller Conference, Nijmegen, September 1981; D. Reinen and C. Friebel, *Inorg. Chem.*, 1983, **23**, 791.

4 C. M. Harris, *Nature (London)*, 1961, **192**, 424.

5 B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 1969, 2219.

6 H. Elliott, B. J. Hathaway, and R. C. Slade, *J. Chem. Soc. A*, 1966, 1443.

7 R. C. Slade, A. A. G. Tomlinson, B. J. Hathaway, and D. E. Billing, *J. Chem. Soc. A*, 1968, 61.

8 R. J. Dudley, B. J. Hathaway, P. G. Hodgson, P. C. Power, and D. J. Loose, *J. Chem. Soc., Dalton Trans.*, 1974, 1005.

9 B. J. Hathaway, D. E. Billing, R. J. Dudley, R. J. Fereday, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 1970, 806.

10 J. Foley, S. Tyagi, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1984, 1.

11 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, Cambridge University, 1976.

12 I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1968, 1678.

13 R. M. Morrison, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, 1980, **58**, 238.

14 R. M. Morrison, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, 1979, **57**, 135.

15 F. S. Stephens, *J. Chem. Soc. A*, 1969, 883, 1248, 2081.

16 B. J. Hathaway, N. Ray, D. Kennedy, N. O'Brien, and B. Murphy, *Acta. Crystallogr., Sect. B*, 1980, **36**, 1371.

17 F. Huq and A. C. Skapski, *J. Chem. Soc. A*, 1971, 1927.

18 F. S. Stephens and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1973, 2293.

19 W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1556.

20 W. D. Harrison, B. J. Hathaway, and D. Kennedy, *Acta Crystallogr., Sect. B*, 1979, **35**, 2301.

21 J. Kaiser, G. Brauer, F. A. Schroder, I. F. Taylor, and S. E. Rasmussen, *J. Chem. Soc., Dalton Trans.*, 1974, 1490.

22 N. Ray, L. Hulett, R. Sheahan, and B. J. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 305.

23 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

24 D. Reinen and C. Friebel, *Struct. Bonding (Berlin)*, 1979, **37**, 1.

25 B. J. Hathaway, M. Duggan, A. Murphy, J. Mullane, C. Power, A. Walsh, and B. Walsh, *Coord. Chem. Rev.*, 1981, **36**, 267.

26 C-C. Chao, *J. Magn. Reson.*, 1973, **10**, 1.

27 B. J. Hathaway, D. E. Billing, R. J. Dudley, R. J. Fereday, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 1970, 806.

28 S. Kremer, H. Stratemeier, and D. Reinen, unpublished work.

29 F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1972, 1350.

30 G. A. Barclay, B. F. Hoskins, C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691.

31 M. Duggan, N. Ray, B. J. Hathaway, A. A. G. Tomlinson, P. Brint, and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.

32 M. Duggan, M. Horgan, J. Mullane, C. P. Power, N. Ray, A. Walsh, and B. J. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 407.

Received 6th September 1983; *Paper* 3/1553