The Single-crystal Electronic and Electron Spin Resonance Spectra of Bis-(2,2′-bipyridylamine)copper(II) Diperchlorate

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The polarised single-crystal electronic spectra and e.s.r. spectra of bis-(2,2′-bipyridylamine)copper(II) diperchlorate have been determined. The in-plane g-values correlate with copper–nitrogen directions and suggest a $d_{x^2-y^2}$ ground state for the compressed tetrahedral CuN_4 chromophore present. The electronic spectra correlate, in the xy-plane with the bisectors of the copper–nitrogen directions; possible reasons for this 45° misalignment of the in-plane g-values and electronic spectral axes are discussed. The electronic spectra are assigned in both C_{2v} and D_2 symmetries (with a preference for the former) and yield the tentative one-electron orbital sequence $d_{x^2-y^2} > d_{xy} > d_{xz} > d_{z^2} > d_{yz}$. Reasons are given for preferring a tetrahedrally distorted square-coplanar description of the stereochemistry of the CuN_4 chromophore of $Cu(bipyam)_2(ClO_4)_2$.

A REGULAR tetrahedral stereochemistry is unknown for complexes of the copper(II) ion,[1] but a number of complexes are available which involve a compressed tetrahedral stereochemistry. This is best known in the $CuCl_4^{2-}$ [2] and $CuBr_4^{2-}$ [3] anions, but also occurs in the CuN_4 chromophore in bis-(αα′-bromodipyrromethene)-copper(II) [4] and bis-(2,2′-bipyridylamine)copper(II) diperchlorate [5] [hereafter referred to as $Cu(bipyam)_2(ClO_4)_2$] and in the CuO_2N_2 chromophores of bis-(*N*-t-butylsalicylaldiminato)copper(II) [6] and bis-(*N*-isopropylsalicylaldiminato)copper(II).[7] In these four complexes a square-coplanar stereochemistry is not possible owing to the steric requirements of the chelate ligands present, consequently these distorted stereochemistries may be alternatively considered as distorted square-coplanar or as distorted tetrahedral. As the N–Cu–N and O–Cu–O angles range [5] from 137 to 145° in these chelate complexes, these represent a larger angular compression than is present in the Cl–Cu–Cl angle of 120° in Cs_2CuCl_4. The polarised single-crystal electronic spectra of Cs_2CuCl_4 have been reported [8] and assigned in D_{2d} symmetry with a d_{xy} ground state, to give a one-electron orbital sequence $d_{xy} > d_{xz}, d_{yz} > d_{x^2-y^2} > d_{z^2}$, an order which reflects the small distortion from a tetrahedral stereochemistry as predicted by crystal-field calculations.[9]

The crystal structure of $Cu(bipyam)_2(ClO_4)_2$ has been reported recently [5] and shown to involve a distorted CuN_4 chromophore and to have a unit cell which is ideal for the measurement of the polarised single-crystal properties. These are now reported.

EXPERIMENTAL

Preparation.—$Cu(bipyam)_2(ClO_4)_2$ was prepared as reported; [10] single crystals were prepared by slow evaporation of a solution of the complex in 4 : 1 water–ethanol.

Physical Methods.—The electronic [11] and e.s.r. spectra [1] were measured as reported previously and the crystal morphology was determined by use of the *X*-ray precession technique.[12]

Crystallographic Data.—$Cu(bipyam)_2(ClO_4)_2$ is monoclinic [5] (space-group $C2/c$) with $a = 9{\cdot}35$, $b = 12{\cdot}88$, $c = 19{\cdot}69$ Å, $\beta = 102{\cdot}8°$, and $Z = 4$. The copper(II) ion has a C_2 site symmetry, but the local CuN_4 chromophore has a distorted tetrahedral stereochemistry of approximately D_{2d} symmetry (Figure 1A). If the two different copper–nitrogen bond-lengths are taken into account the approximate symmetry is C_{2v}. The local molecular axes are defined as shown in Figure 1A. The molecular z-axis is defined as perpendicular to the mean plane of the CuN_4 chromophore and lies parallel to the crystallographic b-axis. The molecular x- and y-axes are then defined as lying approximately in the N(1)–Cu–N(1′) and N(3)–Cu–N(3′) planes respectively. The x-axis is inclined at an angle of 44° to the a-axis and the y-axis at an angle of 46° to the a-axis. The local molecular axes of the four molecules in the unit cell are aligned parallel. The complex is obtained as very dark blue rhombohedra with the (001) face well developed (Figure 1B).

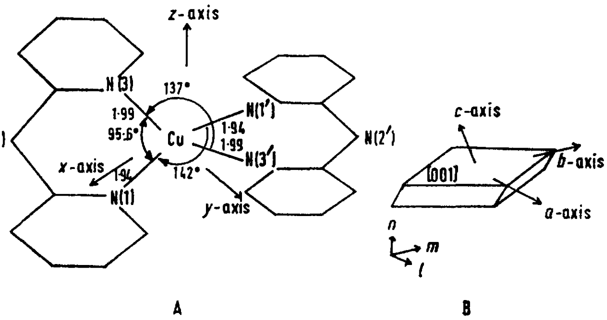

FIGURE 1 $Cu(bipyam)_2(ClO_4)_2$; A, molecular structure; B, crystal morphology

RESULTS

E.s.r. Spectra.—The single-crystal e.s.r. spectra yielded three crystal g-values which are given in Table 1, along with

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[1] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[2] L. Helmnholz and R. F. Kruth, *J. Amer. Chem. Soc.*, 1952, **74**, 1176; M. Bonamico and G. Dessy, *Theoret. Chem. Acta*, 1967, **7**, 367.

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[4] M. Elder and B. R. Penfold, *J. Chem. Soc.* (*A*), 1969, 2556.

[5] J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1971, 2124.

[6] T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 685.

[7] P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, 1966, **88**, 277.

[8] J. Ferguson, *J. Chem. Phys.*, 1964, **40**, 3406.

[9] L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 1963, **2**, 911.

[10] W. R. McWhinnie, *J. Chem. Soc.*, 1964, 5165.

[11] B. J. Hathaway, P. Nicholls, and D. Barnard, *Spectrovision*, 1969, **22**, 4.

[12] M. J. Buerger, ' The Precession Method,' Wiley, New York, 1962.

their direction cosines and those of the co-ordinate axes shown in Figure 1A. As the four molecules in the unit cell have their molecular axes aligned parallel the crystal *g*-values correspond to the molecular *g*-values.

TABLE 1

Cu(bipyam)$_2$(ClO$_4$)$_2$: The direction cosines of A, the single-crystal *g*-values and B, the local molecular axes (Figure 1A)

A		g_3 (2·2438)	g_2 (2·06913)	g_1 (2·05921)
	l	0·0	−0·7660	0·6428
	m	1·0	0·0	0·0
	n	0·0	0·6428	0·7660
B		*z*	*y*	*x*
	l	0·0	−0·6947	0·7193
	m	1·0	0·0	0·0
	n	0·0	0·7193	0·6947

Electronic Spectra.—The reflectance spectrum[10,13] of Cu(bipyam)$_2$(ClO$_4$)$_2$ is unusual in that it gives evidence of four bands in the region 10·0—20·0 kK which could be considered as the four *d–d* transitions theoretically possible for a copper(II) ion. The spectrum consists of a main band at 18·5 kK, with a clear but unresolved shoulder at *ca.* 16·3 kK, a clearly resolved shoulder of medium intensity at 10·6 kK, and some evidence of a weak unresolved shoulder at *ca.* 13·0 kK; values which agree closely with those previously observed[13] for this complex namely, 18·1s, 13·0w, and 10·5w (kK). The polarised single-crystal electronic spectra of Cu(bipyam)$_2$(ClO$_4$)$_2$ (Figure 2) show very marked polarisation and give clear evidence of the four bands indicated in the reflectance spectrum. The *Z*-polarised spectrum was measured in the (001) face parallel to the *b*-axis. The *X*- and *Y*-polarised spectra were obtained by cutting a crystal in the *ac*-plane. The *X*-polarised spectrum was measured parallel to the *a*-axis and the *Y*-polarised spectrum at 90° to the *a*-axis in this *ac*-face. In all cases these directions coincided with the extinction directions. In the *X*- and *Y*-polarised spectra, the measurements were carefully checked to ensure that the maximum polarisation coincided with the crystallographic *a*-axis and the perpendicular to the *ab*-plane respectively. In this notation the *Z*-polarised spectrum coincides with the molecular *z*-axis, but the *X*- and *Y*-spectra were measured in directions at *ca.* 45° to the molecular *x*- and *y*-axes.

The most intense band occurs in *Y*-polarisation at 18·4 kK and has a weak but clearly resolved shoulder at 10·4 kK. The *Z*-polarised spectrum consists of a medium intense band at 15·7 kK with no evidence of a shoulder either to high or low energy. The *X*-polarised spectrum consists of two medium-weak bands of comparable intensity at 18·4 kK and 13·5 kK (with the former most broad) and with some evidence of a very weak band at 10·4 kK.

DISCUSSION

E.s.r. Spectra.—The three single-crystal *g*-values (Table 1) are clearly axial with a small rhombic component and differ appreciably from the isotropic value of 2·07 obtained from a polycrystalline sample.[13] g_3 Is aligned parallel to the *z*-axis of Figure 1A while g_2 and g_1 lie along the projections of the Cu–N(2) and Cu–N(1) bonds on the *xy*-plane, respectively, and suggest a $d_{x^2-y^2}$ ground state rather than the more usual d_{xy} ground state previously assumed[8] for a compressed tetrahedral copper(II) ion environment.* The direction of the lowest *g*-value corresponds with the direction of the shortest copper–nitrogen bond.

Electronic Spectra.—The crystallographic site symmetry[5] of Cu(bipyam)$_2$(ClO$_4$)$_2$ is C_2, but the marked polarisation of the electronic spectra, with a clear difference in the *X*- and *Y*-polarised spectra, suggests a higher symmetry (lacking a centre of symmetry). The local CuN$_4$ chromophore of Cu(bipyam)$_2$(ClO$_4$)$_2$ is approximately D_{2d} or C_{2v} if the difference in the copper–nitrogen bond lengths is taken into account. In D_{2d} symmetry[1] the d_{xz} and d_{yz} orbitals are degenerate and could only be split by spin–orbit coupling. The smallest separation of the four bands (*cf.* Figure 2) is 2·2 kK, which seems rather large to be accounted for by this mechanism, especially as the two bands appear in *Z*- and *X*-polarisation rather than *X*- and *Y*-polarisation. This leaves the point-groups C_{2v} and D_2, the latter of which ignores the copper–nitrogen bond-length difference. On symmetry arguments alone a distorted tetrahedral stereochemistry with C_{2v} symmetry implies a $d_{x^2-y^2}$ ground state, while D_2 symmetry implies a d_{xy} ground state. The former is consistent with the e.s.r. data while the latter is not, but such a criterion is only valid for a basic tetrahedral stereochemistry. If the stereochemistry of Cu(bipyam)$_2$(ClO$_4$)$_2$ is considered to involve a tetrahedral distortion of a square-coplanar stereochemistry such an argument may not be valid (see later). Nevertheless the above arguments suggest that an effective symmetry of C_2 is preferable.

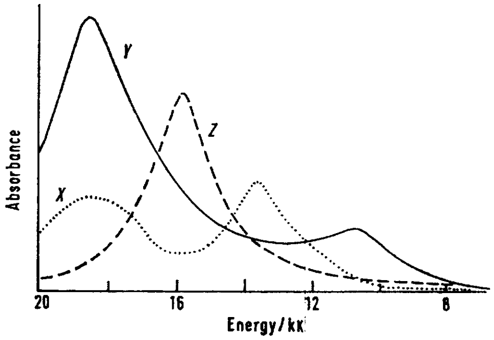

FIGURE 2 The polarised single-crystal electronic spectra of Cu(bipyam)$_2$(ClO$_4$)$_2$; the directions of polarisation are indicated on the curves

Co-ordinate Axes.—One of the more interesting features of the electronic properties of Cu(bipyam)$_2$(ClO$_4$)$_2$ is the observation that the *x*- and *y*-axes of the electronic spectra and the e.s.r. spectra do not coincide, the extent of misalignment being 45°. Theoretically this situation

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* Unfortunately the classic example for a tetrahedral environment for which a d_{xy} ground state has been quoted is Cs$_2$CuCl$_4$,[8] for which no single-crystal e.s.r. evidence for the d_{xy} ground state was presented. In any case the gross misalignment[2] of the four molecules in the unit cell of Cs$_2$CuCl$_4$ would not allow the unequivocal assignment of the electronic ground state. The published spectra may also be assigned in C_{2v} symmetry with a $d_{x^2-y^2}$ ground state and yield the corresponding one-electron orbital sequence $d_{x^2-y^2} > d_{xz} > d_{yz} > d_{xy} > d_{z^2}$.

[13] J. C. Lancaster, W. R. McWhinnie, and P. L. Welham, *J. Chem. Soc.* (*A*), 1971, 1742.

is possible[14] in point-groups of certain symmetries in which the $d_{x^2-y^2}$ and d_{xy} orbitals transform as the same representation and may mix together to form the ground-state configuration. The extent of mixing would determine the degree of misalignment. In practice no clearly described example of such a misalignment has been observed (but see ref. 15). In the point-groups[1] C_{2v} and D_2 the $d_{x^2-y^2}$ and d_{xy} orbitals transform as different representations, namely, A_1 and A_2, and A and B_1 respectively; consequently mixing of these orbitals cannot occur and the observed misalignment of the axes cannot arise through this mechanism.

The polarised single-crystal electronic spectra of $Cu(bipyam)_2(ClO_4)_2$ are undoubtedly dominated by the very intense band at 18·4 kK which could well determine the observed extinction directions in the *ac*-plane. If the observed spectra are purely *d–d* in origin the co-ordinate axes of the electronic spectra would be expected to coincide with the co-ordinate axes of the e.s.r. spectra, but if the observed spectra involved a charge-transfer band, the two sets of co-ordinate axes would not necessarily coincide. In general charge-transfer spectra are more intense than *d–d* spectra and the 18·4 kK band is the one most likely to involve charge-transfer. Even in nitromethane solution saturated with sodium perchlorate the extinction coefficient of the band maximum is only 227, a value much more consistent with an electronically allowed *d–d* transition in a compressed tetrahedral stereochemistry, than a charge-transfer band. Nevertheless the polarisations of the two bands at 13·5 and 10·4 kK were carefully examined in the *ac*-plane to establish whether or not their polarisation directions coincided with that of the 18·4 kK band. In both cases the directions coincided with those of the 18·4 kK band. Consequently there appears to be no justification for considering the 18·4 kK band as a charge-transfer rather than a *d–d* band.

The misalignment of the e.s.r. and electronic axes of $Cu(bipyam)_2(ClO_4)_2$ only occurs in the *xy*-plane, that is, when the crystal is viewed down the *b*-axis of this monoclinic[5] crystal. The possibility that the crystal itself effects the rotation of the electronic axes would only occur if the crystal itself was optically active, but this is ruled out by the presence of a *c*-glide in the space-group *C*2/*c*. In any case such a mechanism for the rotation would require that the rotation were a function of the crystal thickness, whereas the observed misalignment is always 45°.

At present we are unable to offer an adequate explanation of the misalignment of the co-ordinate axes of the electronic and e.s.r. spectra of $Cu(bipyam)_2(ClO_4)_2$; a conclusion which seems to rule out any possibility of assigning the polarised single-crystal electronic spectra. Nevertheless it is considered worthwhile to proceed with an assignment which ignores this misalignment without assuming which type of spectra is misaligned. For this purpose both a $d_{x^2-y^2}$ and a d_{xy} ground state will be considered in both D_2 and C_{2v} symmetry.

Assignment of the Electronic Spectra.—The electronic selection rules for these two symmetries with a $d_{x^2-y^2}$ or d_{xy} ground state have been given previously.[1] With a $d_{x^2-y^2}$ ground state, only one transition is electronically allowed in each polarisation in either symmetry. With a d_{xy} ground state one transition is electronically allowed in both *X*- and *Y*-polarisations in both symmetries but in *Z*-polarisation there are no electronically allowed transitions in C_{2v} symmetry and *two* electronically allowed transitions in D_2 symmetry. The observation of a single relatively intense transition in the *Z*-polarised spectrum of $Cu(bipyam)_2(ClO_4)_2$ seems to rule out the assignment in C_{2v} symmetry with a d_{xy} ground state and only allow its assignment in D_2 symmetry with this ground state if the two electronically allowed transitions ($d_{z^2} \longrightarrow d_{xy}$ and $d_{x^2-y^2} \longrightarrow d_{xy}$) are degenerate, or nearly so, under the band at 15·7 kK. As the latter assignment would leave two *d–d* transitions to be assigned to the three observed bands remaining (18·4, 13·5, and 10·4 kK) it would require that one of these was a charge-transfer band. This possibility was ruled out above, and so the assignment in D_2 symmetry with a d_{xy} ground state is also ruled out. Consequently the assignment in D_2 or C_{2v} symmetry with a d_{xy} ground state will not be considered further.

In *Z*-polarisation with a $d_{x^2-y^2}$ ground state, the band at 15·7 kK is assigned as the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition in C_{2v} symmetry and as the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition in D_2 symmetry (Table 2).

TABLE 2

The assignment of the polarised single-crystal electronic spectra of $Cu(bipyam)_2(ClO_4)_2$ in C_{2v} and D_2 symmetry with a $d_{x^2-y^2}$ ground state

Transition	C_{2v}	D_2
$d_{z^2} \longrightarrow d_{x^2-y^2}$	15·7	10·4
$d_{xy} \longrightarrow d_{x^2-y^2}$	10·4	15·7
$d_{xz} \longrightarrow d_{x^2-y^2}$	13·5	18·4
$d_{yz} \longrightarrow d_{x^2-y^2}$	18·4	13·5
$r_{\parallel}$	0·618	0·759
$r_{\perp}$	0·784	0·784

In order to assign the remaining polarised spectra (Figure 3) it is necessary to label them arbitrarily as *X* and *Y*, and to associate the former with the molecular *x*-axis, the lowest *g*-value direction and the copper–nitrogen(1) direction. The alternative correlation inverts the ordering of the d_{xz} and d_{yz} levels and would result in a less satisfactory understanding of the molecular structure (see later). The band at 18·4 kK in *Y*-polarisation is then assigned as the electronically allowed transition, $d_{yz} \longrightarrow d_{x^2-y^2}$ and $d_{xz} \longrightarrow d_{x^2-y^2}$ in C_{2v} and D_2 symmetries respectively. The very broad band at 18·4 kK in *Y*-polarisation may then be considered as the band in *Y*-polarisation occurring with residual intensity or by a vibronic mechanism, leaving the band at 13·5 kK to be assigned as the electronically allowed transition $d_{xz} \longrightarrow$

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[14] M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, 1969, **50**, 1195; M. A. Hitchman, *J. Chem. Soc.* (*A*), 1970, 4.

[15] B. W. Moores, Ph.D. Thesis, University of Illinois, Urbana, 1968.

$d_{x^2-y^2}$ and $d_{yz} \longrightarrow d_{x^2-y^2}$ in C_{2v} and D_2 symmetries respectively. The weak band at 10·4 kK may then be assigned as the $d_{xy} \longrightarrow d_{x^2-y^2}$ and $d_{z^2} \longrightarrow d_{x^2-y^2}$ transitions in C_{2v} and D_2 symmetries respectively, occurring with vibronic intensity.

These assignments (Table 2) then yield the one-electron orbital sequences; in C_{2v} symmetry: $d_{x^2-y^2} > d_{xy} > d_{xz} > d_{z^2} > d_{yz}$ and in D_2 symmetry: $d_{x^2-y^2} > d_{z^2} > d_{yz} > d_{xy} > d_{xz}$. Of these the former is preferred as it better reflects the molecular symmetry (see earlier).

Orbital Reduction Factors.—By combining the electronic energy levels of Cu(bipyam)$_2$(ClO$_4$)$_2$ with the molecular *g*-values in the appropriate *g*-value expressions[1] the combined spin–orbit and orbital reduction parameters can be evaluated as shown for the two assignments in Table 2. The values are comparable with those normally obtained[1] for CuN$_4$ chromophores and indicate that the tetrahedral distortion has not seriously affected the *r*-values. If these *r*-values are related to the appropriate molecular orbital coefficients, the value of $r_\perp$ is relatively high. This suggests that there is little or no out-of-plane π-bonding but assumes that $r_x \approx r_y$ and in view of the appreciable energy difference between the $d_{xz} \longrightarrow d_{x^2-y^2}$ and $d_{yz} \longrightarrow d_{x^2-y^2}$ transition, namely 4·9 kK, significant differences in r_x and r_y may still be present. As the value of $r_\parallel$ is lower than $r_\perp$, particularly in the preferred assignment in C_{2v} symmetry, this suggests that there may be significant in-plane π-bonding present.

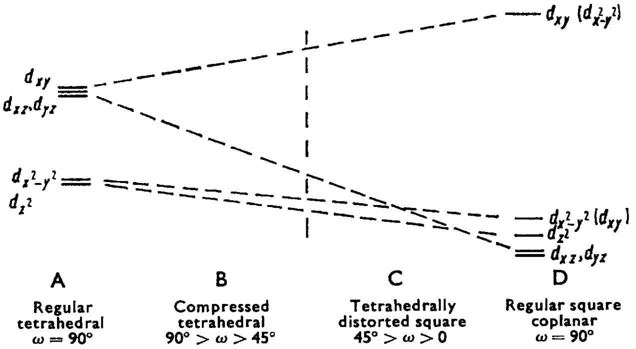

FIGURE 3 The one-electron orbital correlation diagram for a copper(II) ion between a regular tetrahedral, a compressed tetrahedral, a tetrahedrally distorted square-coplanar, and a regular square-coplanar stereochemistry. ω Is the angle between the pairs of ligand atoms

Stereochemistry of Cu(bipyam)$_2$(ClO$_4$)$_2$.—The structure[5] of Cu(bipyam)$_2$(ClO$_4$)$_2$ clearly involves a substantial distortion from either a square-coplanar or tetrahedral stereochemistry. Geometrically, the N–Cu–N bond angles (137·3 and 142·0°) and the angle of 55·6° between the mean planes of the bipyam ligands indicate an intermediate stereochemistry slightly nearer to a tetrahedral description. An alternative criterion is that of the average energy[1] of the *d–d* transitions present. This will be largest for a square-coplanar CuN$_4$ chromophore (*ca.* 20·0 kK) and least for a regular tetrahedral chromophore (*ca.* 5·0—8·0 kK) with a correlation diagram relating the two extremes as shown in Figure 3. The energy maximum of Cu(bipyam)$_2$(ClO$_4$)$_2$ is *ca.* 16—18·0 kK and clearly correlates with a tetrahedral distortion of a square-coplanar chromophore rather than a compressed tetrahedral description. Further support for the former description exists in the $d_{x^2-y^2}$ ground state which is present. If a tetrahedral description predominated, on symmetry grounds this would require a d_{xy} ground state. According to the correlation diagram of Figure 3, the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition should lie highest in energy particularly in the tetrahedral stereochemistry but as it also lies to high energy in the square-coplanar description this provides no clear criterion. [The assignment of the band of lowest energy at 10·4 kK as the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition in D_2 symmetry (Table 2) is a further reason for rejecting this assignment.] A relatively low energy for the $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$ transition could be a better criterion as this transition is most sensitive to the distortion from the regular tetrahedral stereochemistry (Figure 3).

In Cu(bipyam)$_2$(ClO$_4$)$_2$ the d_{xz} and d_{yz} levels are split significantly by 4·9 kK; such a difference suggests that the d_{xz} orbital could be involved in substantial out-of-plane π-bonding despite the observed value of $r_\perp$ of 0·78 and suggests that this average value involves a significant anisotropy in the individual value of r_x and r_y, with the former higher, and the latter lower than $r_\perp$. Such out-of-plane π-bonding *via* the d_{xz} orbital is then reflected in the low energy of the $d_{xz} \longrightarrow d_{x^2-y^2}$ transition, and the relatively short Cu–N(1) bond lengths. Further evidence for the presence of π-bonding to the N(1) ligands but not to the N(2) ligands can be obtained by examination of a molecular model. It can be deduced that if the p_z orbitals on the N(1) ligands are constrained to lie in the *xz*-plane (it being assumed that the nitrogen atoms are sp^2 hybridised) to allow π-bonding to the d_{xz} orbital, the conformation of the chelate ring then twists the p_z orbital on the N(2) ligands through nearly 45°. In this position they cannot π-bond to the d_{yz} orbital, thus exaggerating the difference in bonding to the two pairs of nitrogen ligands.

Less easy to understand is the energy of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition at 10·4 kK. This low energy (relative to the non-bonding $d_{yz} \longrightarrow d_{x^2-y^2}$ orbital) could be understood if there was substantial in-plane π-bonding as suggested by the low value of *r* in C_{2v} symmetry. But with a $d_{x^2-y^2}$ ground state it is impossible to envisage any overlap whatsoever between the d_{xy} orbital and the p_z orbitals on the four-co-ordinated nitrogen atoms to produce π-bonding. A possibility is that the hydrogen atoms at the carbon (6) position of the pyridine rings are in such a position that they interact strongly with the d_{xy} orbital, sufficiently to destabilise it to an energy higher than the d_{xz}, d_{yz}, and d_{z^2} levels, thus lowering the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition. This could also result in the low value observed for $r_\parallel$, which is not due to the presence of π-bonding. An alternative explanation may lie in the differing ground states of compressed tetrahedral (d_{xy}) and tetrahedrally distorted square-coplanar ($d_{x^2-y^2}$) stereochemistries. With increasing tetrahedral distortion of a square-coplanar stereochemistry the energy of the d_{xy} orbital will be increasingly destabilised as it ultimately becomes the ground state in the compressed tetrahedral stereochemistry. In intervening stereochemistries this could result in an anomalously low energy for the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition as observed in the present complex. The relatively low energy of the $d_{x^2-y^2} \longrightarrow d_{xy}$ transition (10·8 kK) in $CaCu(CH_3CO_2)_4,6H_2O$ could also be accounted for in the same way.[16,17]

Conclusion.—Notwithstanding the crystallographic description [5] of the geometry of the CuN_4 chromophore in $Cu(bipyam)_2(ClO_4)_2$ as involving a compressed tetrahedral stereochemistry, the electronic properties are more consistent with a tetrahedrally distorted square-coplanar stereochemistry.

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[16] D. E. Billing, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1970, 1877.

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