Single-crystal Electronic and Electron Spin Resonance Spectra of Four Trigonal Bipyramidal Copper(II) Complexes

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The polarised single-crystal electronic and e.s.r. spectra of four complexes of the copper(II) ion involving a trigonal bipyramidal stereochemistry have been measured. The *g*-factors of each of the complexes correlate with a d_{z^2} ground state and justify a trigonal bipyramidal description of the local molecular stereochemistries. The electronic spectra have been assigned in C_{2v} symmetry and yield one-electron orbital sequences consistent with that predicted by a crystal field model in D_{3h} symmetry, namely $d_{z^2} > d_{x^2-y^2}, d_{xy} > d_{xz}, d_{yz}$. The detailed sequence observed for each complex is interpreted in terms of the local bond lengths and bond angles present and an attempt is made to assess the role of π-bonding in the $Cu(bipy)_2^{2+}$ cation.

THE electronic properties of two trigonal bipyramidal copper(II) complexes, namely diamminecopper(II) trithiocyanatoargentate(I) and iodobis(bipyridyl)copper(II) iodide, have been reported earlier.[1] Both yielded a one-electron orbital sequence which conflicted with the order predicted[2] for the parent D_{3h} symmetry, in which the d_{xz}, d_{yz} level lies below the d_{xy}, $d_{x^2-y^2}$ level. The inversion of these levels in $[Cu(NH_3)_2][Ag(SCN)_3]$ and $[Cu(bipy)_2I]I$ was ascribed[1] to the presence of significant π-bonding from the thiocyanate and iodide ligands, respectively. The crystal structures of four complexes of the copper(II) ion involving trigonal bipyramidal stereochemistries have now been reported; namely, chloro[dodeca(dimethylamino)cyclohexaphosphazene-*NNNN*]copper(II) dichlorocuprate(I),[3] amminebis-(2,2′-bipyridyl)copper(II) tetrafluoroborate,[4] dinitratotrispyridinecopper(II),[5] and monochlorobis(2,2′-bipyridyl)copper(II) chloride hexahydrate[6] {hereafter referred to as $[(dchp)CuCl]CuCl_2$, $[Cu(bipy)_2NH_3][BF_4]_2$, $[Cu(py)_3(NO_3)_2]$, and $[Cu(bipy)_2Cl]Cl,6H_2O$, respectively}. The molecular structures of all four complexes are shown in Figure 1. All four complexes involve ligands with less π-bonding potential than the two complexes previously examined and as the structures of the first three complexes are ideally suited to single-crystal studies[7] (as the axes of the local molecular chromophores are aligned parallel) these have been examined (as described previously[7,8]) and the results are now reported.

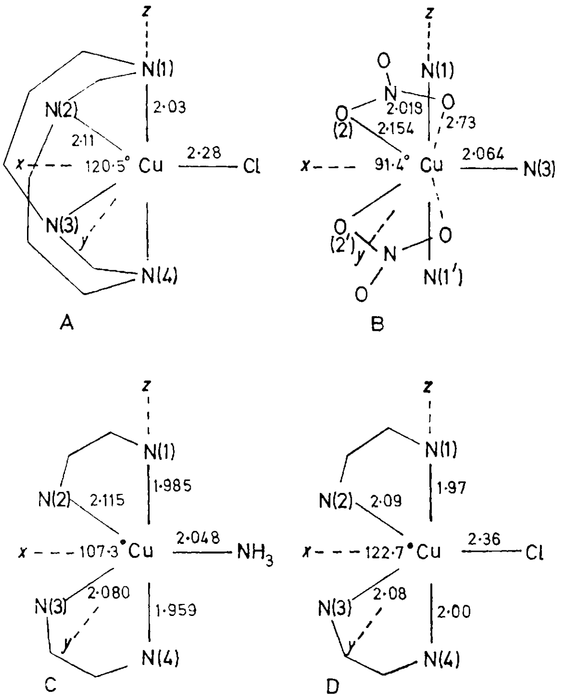

FIGURE 1 The molecular structures of A, $[(dchp)CuCl]CuCl_2$; B, $[Cu(py)_3(NO_3)_2]$; C, $[Cu(bipy)_2NH_3][BF_4]_2$; D, $[Cu(bipy)_2Cl]Cl,6H_2O$

EXPERIMENTAL

Preparation.—Crystals of $[(dchp)CuCl]CuCl_2$ were provided by Professor N. L. Paddock, University of British Columbia, Canada. Crystals of $[Cu(bipy)_2NH_3][BF_4]_2$,[9] $[Cu(py)_3(NO_3)_2]$,[10] and $[Cu(bipy)_2Cl]Cl,6H_2O$[9] were prepared as reported in the literature. Each was satisfactorily characterised by microanalysis and by *X*-ray crystallographic techniques.

RESULTS

Electron Spin Resonance Spectra.—The single-crystal e.s.r. spectra of all four complexes yielded three crystal *g*-factors (Table 1) with no evidence of hyperfine structure. As the local molecular axes in $[(dchp)CuCl]CuCl_2$,[3] $[Cu(bipy)_2NH_3][BF_4]_2$,[4] and $[Cu(py)_3(NO_3)_2]$[5] are aligned parallel the crystal *g*-factors are equivalent to the local molecular *g*-factors,[7] and were observed to lie parallel to the local molecular axes, defined as shown in Figure 1A—C. In each complex the lowest *g*-factor is aligned parallel to the *z*-axes of Figure 1, the intermediate *g*-factor parallel to the *x*-axis, and the highest *g*-factor parallel to the *y*-axis. In $[Cu(bipy)_2Cl]Cl,6H_2O$ the four molecules in the orthorhombic unit cell

[1] B. J. Hathaway, D. E. Billing, R. J. Dudley, R. J. Fereday, and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1970, 806.

[2] P. Day, *Proc. Chem. Soc.*, 1964, 84; W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 841; G. C. Allen and N. S. Hush, *ibid.*, 1967, **6**, 4.

[3] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1482.

[4] F. S. Stephens, *J.C.S. Dalton*, 1972, 1350.

[5] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1972, 1603.

[6] F. S. Stephens and P. A. Tucker, *J.C.S. Dalton*, 1973, 2293.

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

[8] B. J. Hathaway, P. Nicholls, and D. Barnard, *Spectrovision*, 1969, **22**, 4; M. J. Buerger, 'The Precession Method,' Wiley, New York, 1962.

[9] B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1969, 2219.

[10] R. H. Nuttall, A. F. Cameron, and D. W. Taylor, *J. Chem. Soc.* (*A*), 1971, 3103.

have their local y- and z-axes (Figure 1D) misaligned by *ca.* $2\alpha = 78°$ and only the crystal g-factor of 2·1881 is equivalent to a local molecular g-factor, namely g_x. Attempts to resolve these crystal g-factors into the g_z- and g_y-factors (Table 1) proved unsatisfactory and suggested that the misalignment present was nearer to 90° than the 78° obtained by equating the molecular z-axis with the N(1)–Cu–N(4) direction. In view of this uncertainty the resolution was not pursued.

TABLE 1

Crystal g-factors and R-values $[R = (g_2 - g_1)/(g_3 - g_2)]$

	g_z	g_x	g_y	R
$[(\text{dchp})\text{CuCl}]\text{CuCl}_2$	2·0066	2·2024	2·2325	6·5
$[\text{Cu(bipy)}_2(\text{NH}_3)][\text{BF}_4]_2$	2·0146	2·1446	2·2281	1·56
$[\text{Cu(py)}_3(\text{NO}_3)_2]$	2·0250	2·1660	2·2662	1·41
$[\text{Cu(bipy)}_2\text{Cl}]\text{Cl},6\text{H}_2\text{O}$	2·085 *	2·188	2·094 *	

* Resolution (ref. 7) using $2\alpha = 78°$ produced two g-factors of 2·067 and 2·110.

The g-factors for the first three complexes of Table 1 all have their lowest g-factors $<2{\cdot}04$,[7] and their R-values[11] $>1{\cdot}0$, consistent with the unpaired electron occupying a predominantly d_{z^2} orbital consistent with the approximately trigonal bipyramidal stereochemistries present. The term d_{z^2} ground state will be used to describe the electronic ground state of these complexes although it is recognised to be a gross oversimplification of the true ground state wave function, especially for complexes with R-values *ca.* 1·0. As the stereochemistry of $[\text{Cu(bipy)}_2\text{Cl}]\text{Cl},6\text{H}_2\text{O}$ involves the least angular distortion from a regular trigonal bipyramidal stereochemistry it is also assumed to have a predominantly d_{z^2} orbital ground state.

Electronic Spectra.—In each complex the polarised single-crystal electronic spectra were measured at room temperature in a developed face of the crystal or in one obtained by cutting the crystal in the appropriate direction and are shown in Figure 2. All the spectra were recorded with the plane of polarisation parallel to the extinction directions of a particular face, which in most cases corresponded with the projection of the principal g-factors in that face. In the case of the spectra of $[\text{Cu(bipy)}_2\text{NH}_3][\text{BF}_4]_2$ and $[\text{Cu(py)}_3(\text{NO}_3)_2]$ measured in the *ac*-planes of these monoclinic crystals, Figure 3, there is a misalignment of the directions of the g-factors and of the electronic axes of 21 and 20°, respectively. In the former this arises due to the unsymmetrical twisting of the 2'2-bipyridyl ligands about the copper(II) ion [*cf.* $\text{Cu(2,2'-bipyridylamine)}_2(\text{ClO}_4)_2$ in which the misalignment is 45°].[12] In $[\text{Cu(py)}_3(\text{NO}_3)_2]$ the misalignment arises due to the orientation of the plane of the N(3) pyridine ligand (Figure 3B) with respect to the projections of the N(1)–N(1') and O(2)–O(2') directions on to the *ac*-plane. In both complexes as the misalignment is small it is reasonable to associate a given electronic spectrum with the nearest g-factor direction.[12]

Effective Electronic Symmetry.—The crystallographic site symmetries of $[\text{Cu(dchp)Cl}]\text{CuCl}_2$ and $[\text{Cu(py)}_3(\text{NO}_3)_2]$ are C_2 and those of $[\text{Cu(bipy)}_2\text{NH}_3][\text{BF}_4]_2$ and $[\text{Cu(bipy)}_2\text{Cl}]\text{Cl},6\text{H}_2\text{O}$ are C_1. In the former complexes the local molecular x-axes are defined (Figure 1) to lie along the crystallographic C_2 axes, the y- and z-axes are then defined as in Figure 1 to give a consistent set of local molecular axes in all four complexes. In the first three complexes the observation of clearly different spectra in the x-, y-, and z-polarisations, rules out the assignment of the electronic spectra in C_2 symmetry and also in the approximate trigonal bipyramidal symmetries, D_{3h}, D_3, C_{3v}, C_{3h}, and C_3, as x and y are degenerate

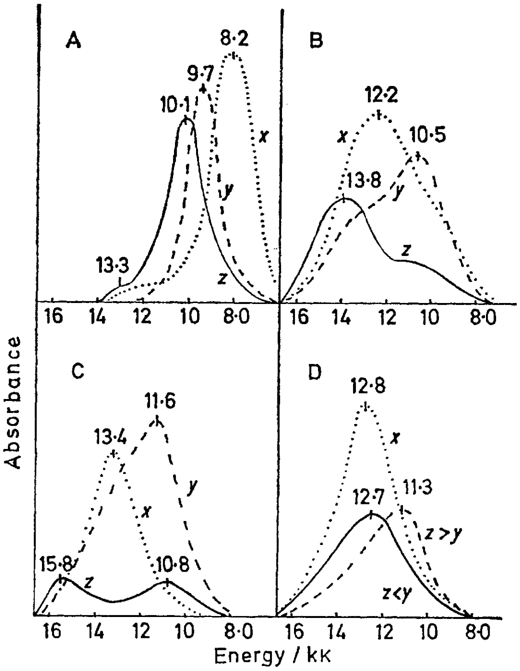

FIGURE 2 The polarised single-crystal room temperature electronic spectra of A, $[(\text{dchp})\text{CuCl}]\text{CuCl}_2$; B, $[\text{Cu(py)}_3(\text{NO}_3)_2]$; C, $[\text{Cu(bipy)}_2\text{NH}_3][\text{BF}_4]_2$; D, $[\text{Cu(bipy)}_2\text{Cl}]\text{Cl},6\text{H}_2\text{O}$

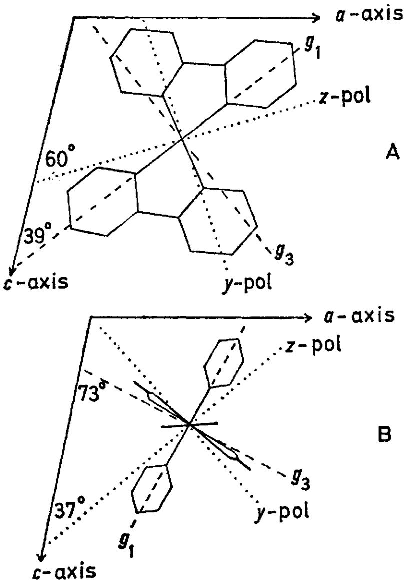

FIGURE 3 The projections of the crystal structures of A, $[\text{Cu(bipy)}_2\text{NH}_3][\text{BF}_4]_2$ and B, $[\text{Cu(py)}_3(\text{NO}_3)_2]$ on to the *ac*-planes of their monoclinic unit cells, showing the relative directions of the g-factors (– – – –) and the extinction directions of the electronic spectra (· · · ·)

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[11] M. A. Hitchman, *J. Chem. Soc.* (*A*), 1970, 4; D. E. Billing, B. J. Hathaway, R. J. Dudley, and A. A. G. Tomlinson, *ibid.*, 1971, 691.

[12] P. G. Hodgson, Ph.D. Thesis, University of Ireland, 1973; R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J.C.S. Dalton*, 1972, 882.

in these symmetries. This only leaves C_{2v} and D_2 symmetries as the possible effective symmetries [7] for these non-centrosymmetric chromophores; of these, the former is preferred as it more clearly relates to the approximate trigonal bipyramidal stereochemistry present in the above three complexes.

Due to the 78° misalignment present in $[Cu(bipy)_2Cl]Cl,6H_2O$ there is little difference in the measured *a*- and *c*-axis crystal spectra, nevertheless, in view of the similarity of the molecular structure to the other three complexes {especially to that of $[Cu(bipy)_2NH_3][BF_4]_2$} it is assumed to have comparable electronic properties.

Assignment of the Electronic Spectra.—The electronic selection rules for a copper(II) ion, with an approximately d_{z^2} ground state, in C_{2v} symmetry with an *x*-principal axis, have been given previously.[1,13] A tentative assignment of the more intense bands in each spectrum as electronically allowed transitions is given in Table 2. Three bands are definitely assigned in $[(dchp)CuCl]CuCl_2$ and $[Cu(py)_3(NO_3)_2]$, two in $[Cu(bipy)_2NH_3][BF_4]_2$ and only one in $[Cu(bipy)_2Cl]Cl,6H_2O$. In $[Cu(bipy)_2NH_3][BF_4]_2$ the *z*-polarised spectrum consists of two weak to medium bands at 15·8 and 10·8 kK either of which could be assigned as the $d_{xz} \longrightarrow d_{z^2}$ transition. In $[Cu(bipy)_2Cl]Cl,6H_2O$ the misalignment of the *y*- and *z*-molecular axes results in two broad bands of medium intensity in the *a*- and *c*-crystal spectra at 11·3 and 12·7 kK respectively. As the latter is more *y*-polarised this suggests that the pure *y*-polarised spectrum would have a band maximum close to 12·7 kK (comparable in energy to the *x*-polarised spectrum) and that the maximum of the *z*-polarised spectrum will lie at lower energy *ca.* 11·2 kK.

TABLE 2

The assignment of the room temperature polarised single-crystal electronic spectra of A, $[(dchp)CuCl]CuCl_2$; B, $[Cu(py)_3(NO_3)_2]$; C, $[Cu(bipy)_2NH_3][BF_4]_2$; and D, $[Cu(bipy)_2Cl]Cl,6H_2O$ in C_{2v} symmetry (*x*-principal axis) and with a d_{z^2} ground state (kK)

Transition		A	B	C		D
$d_{x^2-y^2} \longrightarrow d_{z^2}$	(x)	8·2	12·2	13·4		12·8
$d_{xy} \longrightarrow d_{z^2}$	(y)	9·7	10·5	11·6		{12·7}
$d_{xz} \longrightarrow d_{z^2}$	(z)	10·1	13·8	10·8*	(or 15·8)	{11·2}
$d_{yz} \longrightarrow d_{z^2}$	(vibronic)	13·3		15·8*	(or 10·8)	

* See text.

In C_{2v} symmetry the $d_{yz} \longrightarrow d_{z^2}$ transition is electronically forbidden and can only occur weakly by a vibronic mechanism. In $[(dchp)CuCl]CuCl_2$ there is evidence of a weak fourth band at 13·3 kK, clearly separate from that at 10·1 kK, which is reasonably assigned as the $d_{yz} \longrightarrow d_{z^2}$ transition and yields a complete assignment of the four possible *d*–*d* transitions in a copper(II) complex involving an approximately trigonal bipyramidal stereochemistry. In $[Cu(bipy)_2NH_3][BF_4]_2$ two bands are observed in *z*-polarisation and once the choice of the band to be assigned as the $d_{xz} \longrightarrow d_{z^2}$ transition is made, the second band could be assigned as the $d_{yz} \longrightarrow d_{z^2}$ transition. In $[Cu(py)_3(NO_3)_2]$ and $[Cu(bipy)_2Cl]Cl,6H_2O$ there is no clear evidence of a fourth weak transition.

The assignments of Table 2 yield a complete one-electron orbital sequence of $d_{z^2} > d_{x^2-y^2} > d_{xy} > d_{xz} > d_{yz}$ for $[(dchp)CuCl]CuCl_2$ and partial ones of $d_{z^2} > d_{xz}$ (or d_{yz}) $> d_{xy} > d_{x^2-y^2} > d_{yz}$ (or d_{xz}) for $[Cu(bipy)_2NH_3][BF_4]_2$, of $d_{z^2} > d_{xy} > d_{x^2-y^2} > d_{xz}$ for $[Cu(py)_3(NO_3)_2]$, and the much less certain one of $d_{z^2} > d_{xz} > d_{xy} > d_{x^2-y^2}$ for $[Cu(bipy)_2Cl]Cl,6H_2O$.

DISCUSSION

$[(dchp)CuCl]CuCl_2$.—The one-electron orbital sequence for this complex is consistent with the ordering of the parent D_{3h} levels as predicted [2] by a crystal-field model, namely $d_{z^2} > d_{xy}, d_{x^2-y^2} > d_{xz}, d_{yz}$. This contrasts with the order previously noted [1] for $[Cu(NH_3)_2][Ag(SCN)_3]$ and $[Cu(bipy)_2I]I$, namely, $d_{z^2} > d_{xz}, d_{yz} > d_{xy}, d_{x^2-y^2}$, and which was attributed to the effect of substantial π-bonding by the thiocyanate and iodide ions respectively, and suggesting that there must be significantly less π-bonding in the present complex. This lack of π-bonding effect is consistent with the substantial distortion present in this complex due to the cyclic conformation of the phosphonitrilic ring.[3] Thus N(1) and N(4) are pulled away from the *z*-axis (9·6°) and N(2) and N(3) are lifted out of the equatorial plane by 10°. In addition the chloride ion is a weaker π-bonding ligand than either the iodide or thiocyanate ions. The energies of the electronically allowed transitions in $[(dchp)CuCl]CuCl_2$ are all lower than those of the other complexes of Table 2, an effect which can be attributed to the lower overall crystal-field energy (Δ) due to the different ligand atoms present and to the bond-length and bond-angle distortions described above. In this complex the separation of the d_{xy} and $d_{x^2-y^2}$ orbitals is only 1·5 kK and is in the reverse sense to that observed in $[(Cu(bipy)_2I]I$, $[Cu(bipy)_2NH_3][BF_4]_2$, and $[Cu(py)_3(NO_3)_2]$, an effect which can also be accounted for by the distortion of the N(2) and N(3) nitrogen ligands out of the equatorial plane thus reducing their availability for σ-bonding. The separation of the d_{yz} and d_{xz} orbitals by 3·2 kK is significant as the d_{yz} orbital (at the lower energy) is clearly the least bonding orbital present. The relative destabilisation of the d_{xz} orbital could be accounted for by the angular distortion of the N(1) and N(4) nitrogen ligands, and also by π-bonding to the chloride ligand. The latter is supported by the relatively short copper–chlorine bond length of 2·28 Å which is significantly shorter than that usually associated with an equatorial copper–chlorine bond length in this stereochemistry, namely 2·30—2·40 Å [14] (see Figure 1D).

Bonding in $[Cu(bipy)_2X]$ *Systems*.—Table 3 collects together the structural and electronic data for four complexes involving the $[Cu(bipy)_2X]$ system involving an approximately trigonal bipyramidal or *cis*-distorted octahedral stereochemistry. The molecular geometries of the $Cu(bipy)_2^{2+}$ cation in all four complexes are closely comparable and differ mainly in the N(2)–Cu–N(3) bond angle. Except for the nitrite complex the Cu–X bond lengths are comparable to those normally found for elongated axial copper(II) complexes when the

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[13] I. M. Procter, B. J. Hathaway, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc.* (*A*), 1969, 1192.

[14] F. Huq and A. C. Shapski, *J. Chem. Soc.* (*A*), 1971, 1927.

appropriate ligand bonds in the plane.[7,15] These structural similarities are reflected in the comparable energies of the $d_{x^2-y^2} \longrightarrow d_{z^2}$ and $d_{xy} \longrightarrow d_{z^2}$ transitions, the orbitals which are used in the σ-bonding skeleton of the $Cu(bipy)_2^{2+}$ cation. The low value of the $d_{xy} \longrightarrow d_{z^2}$ transition in the nitrite reflects the exceptional bonding role of the nitrite ion in this complex and has been discussed elsewhere.[13] Less clearly established are the energies of the $d_{xz} \longrightarrow d_{z^2}$ and the $d_{yz} \longrightarrow d_{z^2}$ transitions as the latter can only occur weakly by a vibronic mechanism. The d_{xz} and d_{yz} orbitals can only bond with a π-bonding function, either to the ligand X or to the $Cu(bipy)_2^{2+}$ cation; five factors will then influence this π-bonding.

TABLE 3

Structural and electronic data on $[Cu(bipy)_2X]$ systems (bond lengths in Å, energies in kK)

	$[Cu(bipy)_2(ONO)]NO_3$ [a,b]	$[Cu(bipy)_2NH_3][BF_4]_2$	$[Cu(bipy)_2I]I$ [c]	$[Cu(bipy)_2Cl]Cl,6H_2O$
Cu–N(1)	1·98	1·985	2·03	1·97
Cu–N(2)	2·06	2·115	1·96	2·09
Cu–N(3)	2·10	2·080	2·10	2·08
Cu–N(4)	2·01	1·959	2·00	2·00
Mean Cu–N(1)/Cu–N(4)	1·995	1·978	2·015	1·985
X	O	N	I	Cl
Cu–X	2·27, 2·35	2·048	2·70	2·36
N(2)–Cu–N(3)	102°	107·5°	114°	122·7°
$d_{x^2-y^2} \longrightarrow d_{z^2}$	14·6	13·4	13·8	12·8
$d_{xy} \longrightarrow d_{z^2}$	9·5	11·6	12·7	{12·7}
$d_{xz} \longrightarrow d_{z^2}$	15·0	10·8 (or 15·8)	10·8	{11·2}
$d_{yz} \longrightarrow d_{z^2}$	14·6	15·8 (or 10·8)	9·3 [d]	

[a] Bond lengths in Å, energies in kK. [b] F. Stephens and I. M. Procter, *J. Chem. Soc.* (*A*), 1969, 1248. [c] G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691. [d] See text.

(a) The equatorial N(2)–Cu–N(3) bond angle; when this is 90°, no π-bonding is possible to either the d_{xz} or the d_{yz} orbital from the N(1) and N(4) ligands. As the angle increases to 120° increasing π-bonding to N(1) and N(4) is possible as the atomic *p*-orbitals on the nitrogen atoms (perpendicular to the plane of the bipyridyl ligands) can overlap with the d_{xz} orbital, but the d_{yz} orbital remains non-π-bonding. π-Bonding to the equatorial nitrogen ligands N(2) and N(3) is also considered unlikely, despite the favourable orientation of the *p*-orbitals on these nitrogens in the *xy*-plane, as the d_{xy} and $d_{x^2-y^2}$ orbitals are already involved in σ-bonding. The consistently longer Cu–N bond lengths in the equatorial plane (Table 3) also argue against significant in-plane π-bonding.

(b) The axial Cu–N bond length; the greater the π-bonding to the axial nitrogens the shorter are their lengths; this effect increases in the sequence of complexes: I^- (2·015) < Cl^- (1·985) < NH_3 (1·97).

(c) The π-bonding potential of the in-plane fifth ligand; this is zero for NH_3 and greater for the iodide ion than the chloride ion.

(d) The co-ordination number of the copper(II) chromophore; if this can be increased above that of five by even a weakly co-ordinating sixth ligand then no π-bonding is likely, as in $[Cu(bipy)_2(ONO)]NO_3$, as the total bonding potential is satisfied by σ-bonding.

(e) The size of the fifth ligand; if this is large it may be considered as effectively occupying two co-ordination sites, hence reducing the equatorial N–Cu–N bond angle and hence the out-of-the-*xy*-plane π-bonding of the *p*-orbitals of bipyridyl nitrogen atoms N(1) and N(4).

These various types of bonding are summarised in Table 4. In $[Cu(bipy)_2(ONO)]NO_3$ little or no π-bonding arises from the nitrito-ligand due to the long copper–oxygen bond involved or from bipyridyl N(1) and N(4) nitrogen ligands due to the unfavourable N(2)–Cu–N(3) bond angle of 102°, reflected in the relatively long mean Cu–N(1)/Cu–N(4) bond length of 2·00 Å. Consequently, neither of the d_{xz} and d_{yz} orbitals are involved in π-bonding and the energies of the $d_{xz} \longrightarrow d_{z^2}$ and $d_{yz} \longrightarrow d_{z^2}$ transitions are high and nearly equal and both are higher than the σ-bonding $d_{x^2-y^2} \longrightarrow d_{z^2}$ and $d_{xy} \longrightarrow d_{z^2}$ transitions. In $[Cu(bipy)_2NH_3][BF_4]_2$ π-bonding to the ammonia ligand is impossible, thus encouraging π-bonding to the bipyridyl nitrogen ligands N(1) and N(4) which is reflected in the slightly larger N(2)–Cu–N(3) angle of 107·5° and a shorter mean Cu–N(1)/Cu–N(4) bond length of 1·98 Å. These effects are then reflected in the separation of the d_{yz} and d_{xz} orbitals by 5·0 kK. This would suggest that the $d_{yz} \longrightarrow d_{z^2}$ transition should be assigned as the higher energy band at 15·8 kK as only the d_{xz} orbital can be involved in this type of π-bonding. In $[Cu(bipy)_2I]I$, π-bonding could occur through both the iodide and the axial nitrogen ligands through the d_{xz} orbital, as re-

TABLE 4

The various σ- and π-bonding roles of the *d*-orbitals of the copper(II) ion in the $[Cu(bipy)_2X]$ system. The π-bonding orbitals on the ligand atoms are atomic *p*-orbitals, p_z involves a *p*-orbital orientated with its symmetry axis parallel to the *z*-axes of Figure 1, and $p_{x'},p_{y'}$ are *p*-orbitals orientated in the *xy*-plane of Figure 1 with *x'*, *y'* at 45° to the *x*,*y* axes

C_{2v} Symmetry		σ-Bonding	π-Bonding
d_{z^2}	A_1	N(1) + N(4)	Nil
d_{xy}	B_2	N(2) + N(3) + X	$p_{x'}N(2) + p_{y'}N(3) + p_yX$
$d_{x^2-y^2}$	A_1	N(2) + N(3) + X	$p_{x'}N(2) + p_{y'}N(3) + p_yX$
d_{xz}	B_1	Nil	$p_{x'}N(1) + p_{y'}N(4) + p_zX$
d_{yz}	A_2	Nil	$p_{y'}N(1) + p_{x'}N(4)$

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[15] B. J. Hathaway and P. G. Hodgson, *J. Inorg. Nuclear Chem.*, 1973, 4071.

flected in the low energy of the $d_{xz} \longrightarrow d_{z^2}$ transition. As the iodide is known to be a good π-bonding ligand this type of π-bonding is preferred especially as the mean Cu–N(1)/Cu–N(4) bond length is exceptionally long in this complex, in spite of a more favourable N(2)–Cu–N(3) bond angle of 114°. In this case the $d_{yz} \longrightarrow d_{z^2}$ transition is unlikely to be affected by π-bonding to the iodide ligand as the d_{yz} orbital lies in a plane 90° to the Cu–I bond and its energy should lie above 14·0 kK (and not at 9·3 kK as previously suggested[1] by the dubious technique of gaussian analysis of the low energy electronically allowed band). In [Cu(bipy)$_2$Cl]Cl,6H$_2$O π-bonding could occur through both the chloride and axial nitrogen ligands. The observation of the low mean Cu–N(1)/Cu–N(4) bond length of 1·99 Å and a relatively long Cu–Cl bond length of 2·36 Å suggests that π-bonding to the nitrogen ligands is dominant. This is supported by the presence of the most favourable N(2)–Cu–N(3) angle for π-bonding of 122° and is reflected in the low energy of the $d_{xz} \longrightarrow d_{z^2}$ transition, below that of both the σ-bonding levels which are approximately degenerate at 12·8 kK in this almost regular trigonal chromophore. π-Bonding to the chloride ligand is not ruled out but would be expected to be less than in the case of the iodide ligand.

The above account is considered to be a reasonable rationale of the structural and electronic properties of the Cu(bipy)$_2$X system and shows how π-bonding effects can result in electronic energy level changes of up to 5·0 kK in these systems and supports the original suggestion that π-bonding effects are important in this stereochemistry[1,16] in complexes of the copper(II) ion.

[Cu(py)$_3$(NO$_3$)$_2$].—The energies of the electronically allowed transitions in this complex are comparable to those of [Cu(bipy)$_2$NH$_3$][BF$_4$]$_2$ except that they are 1—2·0 kK lower in energy, consistent with the presence of a CuN$_3$O$_2$ chromophore. The order of the levels is consistent with the crystal-field sequence predicted[2] for a trigonal bipyramidal stereochemistry and the separation of the $d_{x^2-y^2}$ and d_{xy} orbitals may be associated with the relatively small O(2)–Cu–O(2′) angle of 91·4°. Of the ligands present the pyridine ligands are most likely to be involved in π-bonding through the *p*-orbitals in the nitrogen atoms, but as the planes of the pyridine rings are all orientated[5] at *ca.* 45° to the local molecular co-ordinate axes of Figure 1B this type of π-bonding is likely to be very weak if not zero. The oxygen atoms of the nitrate ligands [O(2) and O(2′)] have *p*-orbitals suitably orientated for out-of-the-plane π-bonding, but these oxygen atoms are positioned in a direction at 45° to the *x*- and *y*-axes and, this would make π-bonding to the d_{xz} and d_{yz} orbitals almost impossible. In any case the nitrate ion is a relatively weak ligand[17] and is not usually considered as a good π-bonding ligand, although there is some evidence[18,19] (when it is suitably orientated) for it to be involved in in-plane π-bonding to the copper(II) ion.

While the above results are consistent with a trigonal bipyramidal description of the local stereochemistry of the copper(II) ion in [Cu(py)$_3$(NO$_3$)$_2$] they are not diagnostic of this description. The molecular structure also involves the presence of two further oxygen ligands in the *xy*-plane at 2·73 Å, a distance consistent with semico-ordination[20] of ligands in the elongated octahedral stereochemistry of copper(II) complexes. If these two ligands are considered as weakly bonded then the copper(II) ion is seven-co-ordinate with a pentagonal bipyramidal stereochemistry, CuO$_2$N$_3$O$_2'$. Unfortunately the above electronic data do not allow a distinction to be drawn between these two alternative descriptions as they only differ in the amount of in-plane σ-bonding. All that can be said is that the d_{xy} and $d_{x^2-y^2}$ orbitals are not degenerate, and hence are not equally involved in bonding, but this difference could also be accounted for by the presence of the non-equivalent ligands, the non-equivalent bond lengths, and the small O(2)–Cu–O(2′) angle. The above electronic data do rule out the description of this structure as a square pyramidal stereochemistry, with the Cu–N(3) bond the principal axis with two off-the-*z*-axis oxygen ligands below the *xy*-plane. If this description were correct the largest principal *g*-factor would be orientated along this bond, which it is not. The structure can alternatively be described as an axially elongated stereochemistry with a *y*-principal axis. This possibility cannot be ruled out by the *g*-factors but would require that the electronic spectra should be assigned in D_2 symmetry with a $d_{x^2-y^2}$ ground state, and is inconsistent with the *R*-value of 1·41. For these reasons the description of the stereochemistry of [Cu(py)$_3$(NO$_3$)$_2$] as involving a five-co-ordinated trigonal bipyramidal stereochemistry is preferred.

We thank University College, Cork, for a Senior Demonstratorship (R. J. D.) and a College Demonstratorship (P. G. H.) and the Department of Education for a Studentship (P. C. P.).

[3/1561 *Received, 24th July,* 1973]

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