Crystal and Molecular Structure, Electron Spin Resonance, and Electronic Spectrum of Hexakis(imidazole)copper(II) Nitrate

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The structure of the title compound has been established by three-dimensional *X*-ray crystal-structure analysis from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with $a = 8{\cdot}65(1)$, $b = 17{\cdot}64(1)$, $c = 8{\cdot}38(1)$ Å, $\beta = 93{\cdot}20(10)°$, $Z = 2$. The structure was solved by the heavy-atom approach and molecular parameters were refined by full-matrix least-squares calculations to *R* 0·043 for 2137 independent reflections. The copper atom co-ordination in the centrosymmetric cation is distorted octahedral with Cu–N 2·012(2), 2·049(2), and 2·593(3) Å. In the crystal the nitrate ions bridge the complex cations through N–H ••• O hydrogen bonds, with N ••• O 2·815, 2·897, 3·073, and 3·086 Å. The single-crystal e.s.r. and polarised electronic spectra are also reported and the electronic structure of the chromophore discussed with reference to these and the crystallographic data.

ALTHOUGH the detailed structures of a number of bis- and tetrakis-imidazole copper(II) complexes are known,[1-5] no structural information has been presented for a hexakisimidazolecopper(II) complex. We now report the structure of this cation following an *X*-ray crystallographic study of $[Cu(im)_6][NO_3]_2$ (im = imidazole). Since few single-crystal studies of the electronic properties of compounds containing copper(II) complexed to aromatic *N*-donor ligands have been reported,[6] e.s.r. and electronic spectral information have been obtained for $[Cu(im)_6][NO_3]_2$. These data provide valuable information about the electronic structure of such complexes.

EXPERIMENTAL

Preparation of Hexakisimidazolecopper(II) *Nitrate.*—Bright blue crystals of $[Cu(im)_6][NO_3]_2$ were grown by the slow evaporation of an ethanolic solution of $Cu(NO_3)_2,6H_2O$ and imidazole (1 : 6).

Crystal Data.—$C_{18}H_{24}CuN_{14}O_6$, $M = 596{\cdot}0$, Monoclinic, $a = 8{\cdot}65(1)$, $b = 17{\cdot}64(1)$, $c = 8{\cdot}38(1)$ Å, $\beta = 93{\cdot}20(10)°$, $U = 1282$ Å^3, $D_m = 1{\cdot}54$ (by flotation), $Z = 2$, $D_c = 1{\cdot}543$, $F(000) = 614$. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 15·7 cm^{-1}.

Crystallographic Measurements.—Preliminary cell dimensions and space-group data were obtained from precession and Weissenberg photographs. During these measurements the pale blue crystals were found to decompose slowly on exposure to air. For the intensity measurements a crystal of dimensions 0·3 × 0·2 × 1·2 mm was mounted inside a thin-walled glass capillary and oriented on an Enraf–Nonius CAD 3 diffractometer (Zr-filtered Mo-K_α radiation, take-off angle 3°) with the c^* direction of the crystal coincident with the instrument ϕ axis. Accurate cell parameters were obtained by carefully centring 40 high-angle reflections. All unique reflections to $2\theta = 60°$ were sampled by use of the θ—2θ scanning technique with scan width $(0{\cdot}90 + 0{\cdot}20 \tan \theta)°$. Background measurements were taken on each side of the scan range for a time equal to half the scan period. Two standard reflections measured periodically throughout the course of the data collection showed no significant intensity variation. From these measurements 2137 reflections having $I > 2{\cdot}0\sigma(I)$ were used in the structure analysis. Corrections for Lorentz and polarisation effects, but not for absorption, were applied.

Structure Analysis.—With $Z = 2$ the asymmetric crystal unit consists of one half of the complex ion and one nitrate ion, and the copper atoms are constrained to be at crystallographic centres of symmetry. The copper atom was placed at the origin of the unit cell and held there throughout the course of analysis. Positions for the other non-hydrogen atoms were obtained from the copper-phased three-dimensional electron-density distribution. The structure was refined by full-matrix least-squares calculations at first with isotropic and then with anisotropic temperature factors for all atoms. During the refinement cycles the identity of the unco-ordinated nitrogen atoms of the imidazole ligands became apparent from their relatively lower temperature factors when treated as carbon atoms. At *R* 0·110 a difference Fourier synthesis revealed significant positive electron density at all positions calculated for hydrogen atoms and their inclusion, with $B = 5{\cdot}0$ Å^2, in the next structure-factor calculation reduced *R* to 0·097. Further rounds of least-square adjustment of the non-hydrogen atom parameters brought the refinement to convergence at *R* 0·043.

Final atomic positional and thermal parameters are given in Tables 1 and 2. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21176 (13 pp., 1 microfiche).* Neutral atom scattering factors for copper, carbon, nitrogen, and oxygen were taken from ref. 7 and anomalous dispersion effects for copper were included; values for hydrogen atoms were taken from ref. 8. For the least-squares iterations the weighting scheme used, $\sqrt{w} = 1$ for $|F_o| \leqslant 20{\cdot}0$ and $\sqrt{w} = 20{\cdot}0/|F_o|$ for $|F_o| > 20{\cdot}0$, showed no systematic dependence of $\langle w\Delta^2\rangle$ in ranges of $|F_o|$ and $\sin \theta$.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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TABLE 1

Fractional atomic co-ordinates ($\times 10^5$) and anisotropic temperature factor parameters,* with estimated standard deviations in parentheses

	x	y	z	10^4b_{11}	10^5b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}
Cu	0(—)	0(—)	0(—)	54(0·4)	291(2)	79(0·5)	−23(0·6)	−7(0·8)	35(0·6)
N(1A)	−469(3)	1340(2)	1151(3)	104(4)	303(10)	113(4)	8(3)	45(6)	2(3)
C(2A)	−1918(4)	1512(2)	1408(4)	113(4)	315(12)	133(5)	18(4)	41(8)	7(4)
N(3A)	−2000(4)	1972(2)	2662(4)	137(4)	366(12)	216(6)	33(4)	126(8)	−38(4)
C(4A)	−526(6)	2106(3)	3261(6)	174(7)	379(15)	201(7)	−12(5)	62(12)	−75(5)
C(5A)	395(4)	1722(2)	2324(5)	107(4)	265(11)	158(5)	−13(4)	38(9)	−8(4)
N(1B)	2020(3)	−127(1)	1370(3)	68(3)	227(9)	87(3)	−2(2)	−5(5)	3(8)
C(2B)	2330(4)	−707(2)	2336(4)	97(4)	213(10)	126(5)	8(3)	−30(7)	0(4)
N(3B)	3771(3)	−671(2)	2987(4)	103(4)	288(9)	135(4)	40(3)	−44(7)	9(3)
C(4B)	4433(4)	−28(3)	2431(5)	60(3)	427(14)	164(5)	2(5)	−26(7)	18(6)
C(5B)	3343(4)	307(2)	1429(4)	62(4)	338(11)	133(5)	−1(4)	4(7)	15(4)
N(1C)	1135(3)	439(1)	−1817(3)	65(3)	212(7)	81(3)	−13(3)	−4(5)	14(3)
C(2C)	1743(3)	1124(2)	−1893(4)	81(3)	226(10)	99(4)	−14(3)	30(6)	3(3)
N(3C)	2261(3)	1251(2)	−3343(3)	88(3)	241(8)	119(4)	−12(3)	37(6)	28(3)
C(4C)	1979(4)	622(2)	−4251(4)	98(5)	324(14)	85(4)	13(4)	21(8)	13(4)
C(5C)	1283(4)	120(2)	−3305(4)	82(4)	218(12)	92(4)	−5(4)	−14(7)	2(4)
N	4626(4)	2419(2)	4600(4)	84(4)	311(11)	150(5)	−6(4)	20(7)	52(4)
O(1)	3441(3)	2576(2)	5300(4)	155(4)	342(9)	315(6)	48(3)	229(7)	97(4)
O(2)	5120(4)	1761(2)	4631(4)	212(5)	359(10)	219(5)	72(4)	158(8)	64(4)
O(3)	5285(4)	2902(2)	3841(4)	152(4)	454(11)	314(6)	−42(4)	105(8)	114(4)

* In the form $B \sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$.

Electron Spin Resonance Spectra.—E.s.r. spectra were recorded in the crystallographic a^*b, bc, and a^*c planes at room temperature and *ca.* 160 K by methods outlined previously.[9] In agreement with the monoclinic symmetry of the system the e.s.r. spectra at both temperatures consisted of two-line systems in the a^*b and bc planes, one from each of the two magnetically inequivalent molecules, and only a single line in the a^*c plane. Copper hyperfine structure was only partially resolved when the direction of the applied magnetic field was within *ca.* 30° of the b axis. At all other orientations no such structure was resolved. Cooling the crystal to 160 K did not significantly alter the resolution. In view of this, no attempt has been made to estimate the copper hyperfine coupling constants. The data obtained have been treated by the method of Schonland [10] to give the principal molecular g values and their orientations with respect to the crystal axes (see later Table 7). Of the two alternative sets of g values given by this treatment, we have chosen the one with directions corresponding closest to those calculated from the crystallographic data for the Cu–N direction.

TABLE 2

Calculated fractional atomic co-ordinates ($\times 10^3$) for hydrogen atoms, labelled according to the atom to which they are bonded

	x	y	z
H(2A)	−288	131	72
H(3A)	−301	219	312
H(4A)	−20	244	426
H(5A)	92	205	146
H(2B)	155	−114	256
H(3B)	431	−106	378
H(4B)	556	17	272
H(5B)	299	81	197
H(2C)	181	152	−95
H(3C)	279	175	−372
H(4C)	225	54	−544
H(5C)	68	−31	−275

Single-crystal Polarised Electronic Spectra.—Absorption spectra were recorded at room temperature on a Cary 14 spectrophotometer equipped with Nicol prisms for single crystals mounted on glass microscope slides in orientations suitable to permit the electric vector of the incident beam to be polarised parallel to the crystal b axis and parallel to selected directions in the a^*c plane. For the latter, spectra were recorded with the electric vector polarised parallel to the a^* or c crystal axes and also parallel to the extinction directions of the a^*c plane, which are inclined at *ca.* 30° to the crystal axes. Each of these last-named spectra were found to resemble closely that obtained with the electric vector polarised parallel to that axis nearest to the extinction direction. Figure 1 summarises the spectra recorded with the electric vector of the incident beam polarised along the a^*, b, and c crystal directions.

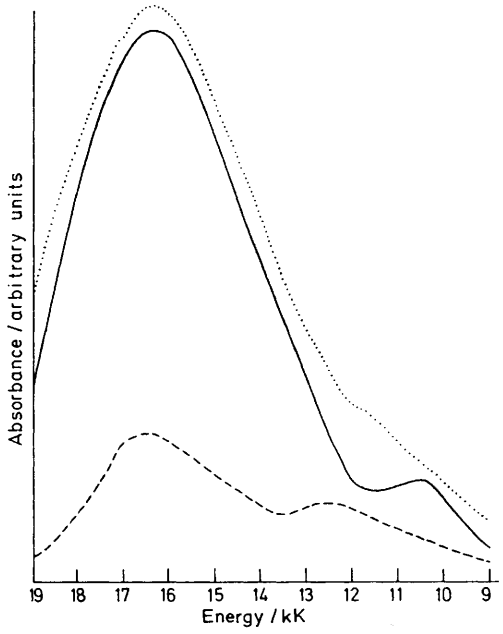

FIGURE 1 Electronic spectra recorded with the electric vector of the incident light polarised parallel to the a^* (full line), b (dashed line), and c (dotted line) crystal axes

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[9] C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, 320.

[10] D. S. Schonland, *Proc. Phys. Soc.*, 1959, **73**, 788.

Crystal-field Calculations.—Values for the molecular g values and the energies of the d–d transitions for the CuN_6 chromophore were calculated by the procedure outlined previously.[11] The d orbital separations were estimated by solving the secular determinant resulting from the perturbation of the free-ion ^2D funtions by the potential $V_{D_{2h}} + k\zeta\hat{l}\,.\,\hat{s}$ (ζ is the single electron spin–orbit coupling constant taken [12a] to be -828 cm^{-1}, and k the orbital reduction factor which was allowed to be anisotropic, $k_x \neq k_y \neq k_z$). Solution of the secular equations and substitution in expressions (1)—(3) (where $\psi_g\pm$ refer to the ground d state eigenfunc-

$$g_z = 2\langle\psi_g + |k_z\hat{l}_z + 2{\cdot}0023\,\hat{s}_z|\psi_g+\rangle \qquad (1)$$

$$g_x = 2\langle\psi_g + |k_x\hat{l}_x + 2{\cdot}0023\,\hat{s}_x|\psi_g-\rangle \qquad (2)$$

$$g_y = 2i\langle\psi_g + |k_y\hat{l}_y + 2{\cdot}0023\,\hat{s}_y|\psi_g-\rangle \qquad (3)$$

tions which are predominantly associated with $m_s = \pm\frac{1}{2}$) afforded the principal molecular g value.

RESULTS AND DISCUSSION

Crystal and Molecular Structure.—The co-ordination geometry in the complex cation and the atom numbering are shown in Figure 2. A view of the crystal structure seen in projection along the b axis is illustrated in Figure 3. The crystals contain centrosymmetric $[Cu(im)_6]^{2+}$ cations and pairs of nitrate anions related by an inversion centre. Interatomic distances and valency angles are listed in Table 3, torsion angles around the copper–nitrogen bonds are in Table 4, and displacements of some atoms from least-squares planes through groups of atoms are in Table 5.

The copper atom lies on a crystallographic centre of symmetry and is surrounded by six imidazole ligands in a tetragonally distorted octahedral arrangement where the copper atom is required by symmetry to lie in the basal plane defined by N(1B), N(1C) and centrosymmetrically related N(1B′), N(1C′). Equatorial Cu–N(1B) [2·049(2)] and Cu–N(1C) [2·012(2) Å] distances are approximately equal and similar to corresponding lengths in $[Cu(im)_4]I_2$,[1] 1·98—2·04, in $[Cu(im)_4(CH_3OCH_2CO_2)_2]$,[2] 1·91—2·05,

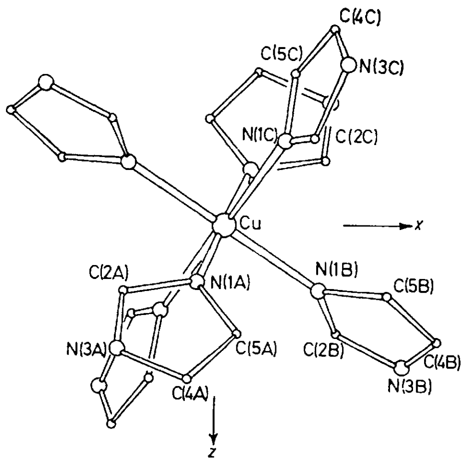

FIGURE 2 Atom arrangement in the $[Cu(im)_6]^{2+}$ ion

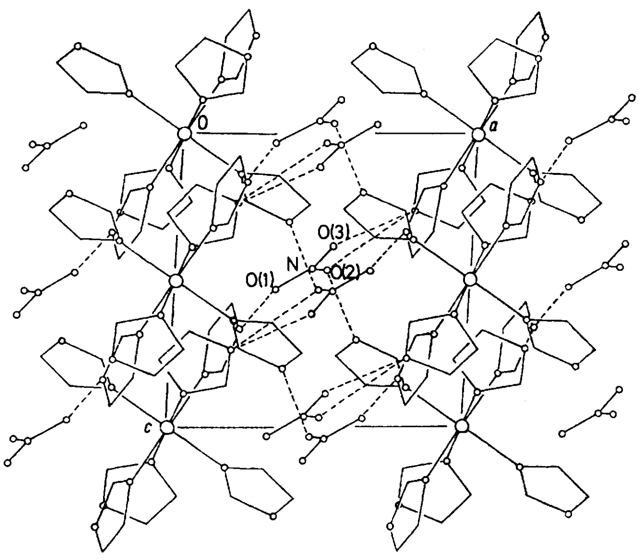

FIGURE 3 Crystal structure of $[Cu(im)_6][NO_3]_2$ viewed in projection along the b axis; hydrogen bonds are denoted by broken lines

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths

Cu–N(1A)	2·593(3)	N(3B)–C(4B)	1·363(5)
Cu–N(1B)	2·049(2)	C(4B)–C(5B)	1·362(5)
Cu–N(1C)	2·012(2)	N(1C)–C(2C)	1·321(4)
N(1A)–C(2A)	1·319(5)	N(1C)–C(5C)	1·381(4)
N(1A)–C(5A)	1·378(5)	C(2C)–N(3C)	1·337(4)
C(2A)–N(3A)	1·333(5)	N(3C)–C(4C)	1·361(5)
N(3A)–C(4A)	1·365(6)	C(4C)–C(5C)	1·352(5)
C(4A)–C(5A)	1·334(6)	N–O(1)	1·241(5)
N(1B)–C(2B)	1·322(4)	N–O(2)	1·237(5)
N(1B)–C(5B)	1·375(4)	N–O(3)	1·223(5)
C(2B)–N(3B)	1·333(4)		

(*b*) Valency angles

N(1A)–Cu–N(1B)	92·2(1)	C(2B)–N(3B)–C(4B)	107·5(3)
N(1A)–Cu–N(1C)	91·4(1)	N(3B)–C(4B)–C(5B)	106·4(3)
N(1B)–Cu–N(1C)	91·7(1)	N(1B)–C(5B)–C(4B)	109·1(3)
Cu–N(1A)–C(2A)	116·1(2)	Cu–N(1C)–C(2C)	126·9(2)
Cu–N(1A)–C(5A)	128·4(2)	Cu–N(1C)–C(5C)	126·9(2)
C(2A)–N(1A)–C(5A)	104·7(3)	C(2C)–N(1C)–C(5C)	105·8(3)
N(1A)–C(2A)–N(3A)	111·3(3)	N(1C)–C(2C)–N(3C)	110·6(3)
C(2A)–N(3A)–C(4A)	107·8(3)	C(2C)–N(3C)–C(4C)	108·2(3)
N(3A)–C(4A)–C(5A)	105·8(4)	N(3C)–C(4C)–C(5C)	106·2(3)
N(1A)–C(5A)–C(4A)	110·5(4)	N(1C)–C(5C)–C(4C)	109·2(3)
Cu–N(1B)–C(2B)	124·4(2)	O(1)–N–O(2)	119·6(4)
Cu–N(1B)–C(5B)	129·9(2)	O(1)–N–O(3)	120·8(4)
N(2B)–N(1B)–C(5B)	105·6(3)	O(2)–N–O(3)	119·7(3)
N(1B)–C(2B)–N(3B)	111·5(3)		

(*c*) Hydrogen bonded distances

O(1) · · · N(3C^{II})	2·815	O(3) · · · N(3A^{I})	3·073
N(3B) · · · O(2^{III})	2·897	O(2) · · · N(3A^{I})	3·086

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I $1 + x, y, z$ II $x, y, 1 + z$ III $1 - x, -y, 1 - z$

TABLE 4

Torsion angles (°) around the Cu–N bonds

N(1B)–Cu–N(1A)–C(2A)	−142	N(1C)–Cu–N(1B)–C(2B)	−142
N(1B)–Cu–N(1A)–C(5A)	−3	N(1C)–Cu–N(1B)–C(5B)	33
N(1C)–Cu–N(1A)–C(2A)	126	N(1A)–Cu–N(1C)–C(2C)	18
N(1C)–Cu–N(1A)–C(5A)	−95	N(1A)–Cu–N(1C)–C(5C)	−154
N(1A)–Cu–N(1B)–C(2B)	126	N(2A)–Cu–N(1C)–C(2C)	−74
N(1A)–Cu–N(1B)–C(5B)	−59	N(2A)–Cu–N(1C)–C(5C)	114

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[11] C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

[12] (*a*) F. E. Mabbs and W. R. Smail, *J. Chem. Soc.* (*A*), 1970, 1716; (*b*) R. J. Dudley and B. J. Hathaway, *ibid.*, 1971, 1442.

$Cu(im)_4SO_4$,[3] 2·00—2·02, and in $[Cu(im)_4(ClO_4)_2]$,[4] 1·997—2·007 Å. The axial Cu–N length [2·593(3) Å] exceeds the mean of the equatorial distances (2·031 Å) by an amount similar to that found for several other six-co-ordinate copper(II) complexes involving nitrogen donor atoms; the equatorial-to-axial length ratio of 0·78 is close to a calculated mean of *ca.* 0·8 for a number of such complexes.[13]

TABLE 5

(*a*) Equations of least-squares planes in the form $AX + BY + CZ + D = 0$,* and, in square brackets, displacements (Å) of some atoms from the planes

Plane (*A*): N(1A), C(2A), N(3A), C(4A), C(5A)

$$0{\cdot}0869X + 0{\cdot}7942Y - 0{\cdot}6014Z - 1{\cdot}2598 = 0$$

[Cu −1·260, N(1A) −0·002, C(2A) 0·000, N(3A) 0·002, C(4A) −0·004, C(5A) 0·004]

Plane (*B*) : N(1B), C(2B), N(3B), C(5B)

$$0{\cdot}3768X - 0{\cdot}5179Y - 0{\cdot}7680Z + 0{\cdot}1331 = 0$$

[Cu 0·133, N(1B) 0·003, C(2B) −0·004, N(3B) 0·003, C(4B) −0·001, C(5B) −0·001]

Plane (*C*): N(1C), C(2C), N(3C), C(4C), C(5C)

$$-0{\cdot}8780X + 0{\cdot}3684Y - 0{\cdot}3054Z + 0{\cdot}1874 = 0$$

[Cu 0·187, N(1C) 0·000, C(2C) 0·000, N(3C) 0·000, C(4C) 0·000, C(5C) 0·000]

Plane (*D*): N(1), O(1), O(2), O(3)

$$-0{\cdot}5258X - 0{\cdot}2223Y - 0{\cdot}8211Z + 6{\cdot}0893 = 0$$

[N(1) −0·010, O(1) 0·003, O(2) 0·003, O(3) 0·003]

(*b*) Dihedral angles (°) between the planes

(*A*)–(*B*) 85·2 (*A*)–(*C*) 66·4 *B*(*C*)–(*C*) 106·7

* Cartesian co-ordinates (*X*, *Y*, *Z*) are related to the fractional co-ordinates (*x*, *y*, *z*) by the transformation $[X, Y, Z] = [xa + zc \cos\beta, yb, xc \sin\beta]$.

The imidazole rings are planar (Table 5). Their individual bond lengths do not depart significantly from their respective means values and correspond well with those found in free imidazole[14] at −150 °C, and with those reported for this neutral ligand in other complexes.[15-18]

In other divalent metal complexes of the type $[M(im)_6][NO_3]_2$($M =$ Co, Ni, or Cd) which have been studied previously,[16-18] the complex cation has $\bar{3}$ point symmetry and therefore the metal forms six equally strong bonds to the imidazole nitrogen atoms at distances in the range 2·13—2·36 Å. In contrast to these, the d^9 configuration of the metal in the present copper(II) complex presumably results in the four short (equatorial) and two long (axial) metal–nitrogen bond lengths, a stereochemistry common for copper(II).[13] Whereas the copper atom is constrained by symmetry to lie in the basal plane defined by four bonded imidazole nitrogen atoms (*vide supra*), it is not required to lie in these imidazole ring planes and, in fact, it is found to be displaced significantly from each (Δ 0·133, 0·188 Å). In the case of the more weakly co-ordinated axial ligands there is an even greater displacement from the ring plane (Δ 1·261 Å), corresponding to 30° out-of-plane bending of the Cu–N(1A) bond. This large departure from planarity and the unequal Cu–N(1A)–C(2A) (128·4) and Cu–N(1A)–C(5A) (116·1°) valency angles, are due to tilting of the axial ligand about the Cu–N(1A) bond in order that N(3A) may participate in a bifurcated hydrogen bond to an adjacent nitrate ion [N(3A)–H · · · O(3) 3·073 and N(3A)–H · · · O(2) 3·086 Å]. The imidazole groups containing the basal nitrogen atoms have significantly different orientations with respect to the plane defined by the copper and the four basal nitrogen atoms. The plane of the imidazole groups containing the atom N(1C) [Cu–N(1C) was chosen to define the *x* axis for the complex] makes an angle of 70·1° with the CuN_4 plane. In contrast to this, the plane of the imidazole group containing N(1B) [Cu–N(1B) was chosen to define the *y* axis] makes an angle of 35·6° with the CuN_4 plane. Thus, if the nitrogen atoms N(1C) and N(1B) are to be involved in π bonding with the metal *d* orbitals, the p_π orbital of N(1C) is more favourably disposed for π bonding with d_{xy} than with d_{xz}, whereas that of N(1B) should overlap with d_{yz} more than with d_{xy}. The extent of overlap with the metals π orbitals is therefore expected to decrease as $d_{xy} > d_{yz} > d_{xz}$ (*vide infra*).

Nitrate ion oxygen atoms are also involved in the two other hydrogen bonds to neighbouring complex cations [N(3C)–H · · · O(1) 2·815, and N(3B)–H · · · O(2) 2·897 Å], thereby fully utilising the N–H hydrogen atom donors to produce an extensive hydrogen bonded arrangement (Figure 3). The nitrate ions are planar, as expected, and none of the individual N–O lengths differs significantly from the mean (1·236 Å) which lies in the normal range found for this ion.

Electronic Structure.—Assuming that the gross symmetry of the CuN_6 arrangement will be the most important factor in determining the electronic structure of the chromophore, we have interpreted the electronic structure on the basis of D_{2h} rather than the more nearly correct C_{2h} symmetry.

TABLE 6

Assignment of the electronic spectrum

Transition	Selection rules *			Exptl. band max/kK
	x	*y*	*z*	
$d_{xy} \rightarrow d_{x^2-y^2}$	A	A	F	10·7
$d_{z^2} \rightarrow d_{x^2-y^2}$	A	A	A	12·5
$d_{xz} \rightarrow d_{x^2-y^2}$	A	F	A	16·2
$d_{yz} \rightarrow d_{x^2-y^2}$	F	A	A	

* Determined for D_{2h} symmetry. The electric vector of the incident light polarised parallel to the given molecular direction assuming vibronic coupling with the vibrational modes of the CuN_6 skeleton. A = allowed, F = forbidden.

Because the molecules are not all oriented in the same manner and the *d–d* transitions are only vibronically allowed, an unambiguous assignment of the spectra (Figure 1) is difficult. However, a suggested assignment is presented in Table 6, the *d* orbital sequence $d_{x^2-y^2} >$

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$d_{xy} > d_{z^2} > d_{xz},d_{yz}$ * being the same as determined for other nearly square-planar copper(II) systems.[9,12] In agreement with the selection rules, the strong band centred at 16·2 kK † which appears in all polarisations is attributed to the unresolved components of the $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions. Since the $d_{xy} \rightarrow d_{x^2-y^2}$ transition is forbidden in molecular z polarisation (*i.e. ca.* the crystal b direction, see direction cosines in Table 7), whereas the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is allowed in this polarisation, we favour the assignment of the band at 12·5 kK to this latter transition. The selection rules indicate that the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition should also appear in the other two polarisations; it may do so but it is much less evident than in b polarisation. The weak maximum which occurs in a^* polarisation at 10·7 kK is assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition; although it is also expected for c polarisation, this transition is, however, not discernible. This assignment leaves the poorly defined shoulders at 17·2 and 11·7 kK unaccounted for. The former could be the higher-energy component of the $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ transitions but it is difficult to understand why it should only appear as a weak shoulder. There seems to be no explanation of the 11·7 kK feature in terms of a d–d transition.

TABLE 7

Molecular g values and their directions with respect to the crystal axes

	Set 1				Set 2		
(*a*) 293 K g value	c	b	a^*	g value	c	b	a^*
2·039 ± 0·002	41° 25′	69° 43′	55° 42′	2·048 ± 0·001	26° 5′	67° 22′	77° 44′
2·068 ± 0·002	56° 46′	81° 19′	34° 40′	2·059 ± 0·001	76° 31′	41° 48′	13° 30′
2·275 ± 0·001	68° 16′	22° 12′	85° 36′	2·276 ± 0·001	68° 7′	22° 39′	84° 36′
(*b*) 160 K g value				g value			
2·039 ± 0·002	38° 1′	69° 6′	59° 52′	2·039 ± 0·002	38° 5′	69° 8′	60° 0′
2·059 ± 0·003	59° 57′	84° 6′	30° 46′	2·059 ± 0·003	60° 9′	84° 15′	30° 46′
2·273 ± 0·003	69° 0′	21° 48′	84° 24′	2·273 ± 0·003	69° 0′	21° 48′	84° 25′
(*c*) Molecular axes							
Cu–N(1C) x	40° 37′	66° 16′	59° 25′				
Cu–N(1B) y	59° 53′	86° 25′	30° 30′				
Cu–N(1A) z	67° 36′	23° 24′	83° 36′				

Errors quoted on g values represent range found for the two inequivalent molecules in the unit cell.

A modified crystal-field approach[11] was adopted to estimate values for the d–d transition energies and the molecular g values. Initially the former were calculated by varying the Dq and Cp values for the nitrogen atoms N(1C) and N(1C′) nearest to the copper and scaling the values for the other four donor atoms according to the metal-atom separation (r) and $1/r^5$ (Dq) and $1/r^3$ (Cp).[12] Within this framework the parameters which gave a reasonable fit to the observed spectral energies were $-Dq$ 1000—1200 cm^{-1} and $-Cp$ 4500—5500 cm^{-1}. The best fit was considered to be for $-Dq$ 1100 and $-Cp$ 5000 cm^{-1}, and these parameters were used to find the values of k which gave agreement between the measured (Table 7) and calculated molecular g values to within three times the estimated experimental error. The results of a selection of calculations are presented in Table 8. Such results suggested that the magnitude of the orbital-reduction factors varies as $k_z < k_x \leqslant k_y$.

In the D_{2h} point group, where there is no metal d–p orbital mixing, the values of k can be related to the coefficients of the d orbitals in the copper antibonding molecular orbitals. The relationships are (4)—(6), where α, β, δ, γ_1, and γ_2 are the coefficients of the $d_{x^2-y^2}$,

$$k_z = \alpha\beta \tag{4}$$

$$(a - \sqrt{3}b)k_x = (a\alpha - \sqrt{3}b\delta)\gamma_1 \tag{5}$$

$$(a + \sqrt{3}b)k_y = (a\alpha + \sqrt{3}b\delta)\gamma_2 \tag{6}$$

d_{xy}, d_{z^2}, d_{yz}, and d_{xz} orbitals, and a and b are related by $(x^2 - y^2) = a_{d_{x^2-y^2}} - b_{d_{z^2}}$ with $a^2 + b^2 = 1$. In the absence of $d_{x^2-y^2}$ — d_{z^2} orbital mixing the k values give

TABLE 8

Crystal-field parameters *

$-Dq$/ cm^{-1}	$-Cp$/ cm^{-1}	Energy sepn. ($\times 10^{-3}$ cm^{-1}) from $d_{x^2-y^2}$ ground-state			
		Δ_{xy}	Δ_{z^2}	Δ_{xz}	Δ_{yz}
1000	5000	9·68	11·94	14·98	16·08
1000	5500	9·69	12·94	15·72	16·87
1000	6000	9·70	13·93	16·46	17·67
1100	4500	10·60	11·16	15·01	16·01
1100	5000	10·62	12·16	15·75	16·80
1100	5500	10·63	13·16	16·48	17·59
1200	4000	11·53	10·36	15·05	15·96
1200	4500	11·56	11·36	15·78	16·74
1200	5000	11·56	12·38	16·51	17·52
1300	4000	12·46	10·60	15·85	16·47
1300	4500	12·47	11·61	16·58	17·25
1300	5000	12·48	12·63	17·32	18·03

			Calc. g values with Dq −1100 and Cp −5000 cm^{-1}		
k_x	k_y	k_z	g_x	g_y	g_z
0·80	0·80	0·65	2·046	2·070	2·254
0·80	0·80	0·68	2·045	2·069	2·279
0·80	0·80	0·70	2·045	2·069	2·296
0·72	0·80	0·68	2·037	2·066	2·280
0·74	0·80	0·68	2·039	2·066	2·280
0·74	0·80	0·67	2·039	2·067	2·271
0·76	0·80	0·68	2·041	2·067	2·280
0·78	0·80	0·68	2·043	2·068	2·279
0·78	0·78	0·68	2·042	2·066	2·279
0·74	0·78	0·68	2·039	2·064	2·280
0·74	0·82	0·68	2·040	2·069	2·279
0·72	0·82	0·68	2·038	2·069	2·280

* The parameters Dq and Cp refer to Cu–N 2·012 Å.

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* The x and y molecular axes are rotated 45° with respect to those used in refs. 9 and 12.

† 1 kK = 10^3 cm^{-1}.

$\beta < \gamma_1 \leqslant \gamma_2$. Since the d_{xy}, d_{yz}, and d_{xz} are metal π orbitals in this system, the relative magnitude of the coefficients indicate that the admixture of the ligand p_π orbitals with the metal d_π orbitals varies as $d_{xy} > d_{yz} \geqslant d_{xz}$. This variation correlates well with the observed orientations of the planes of the imidazole groups containing the basal nitrogen atoms described earlier. Taking account of $d_{x^2-y^2} - d_{z^2}$ mixing does not affect the relative ordering with respect to d_{xy} but the relative positions of d_{yz} and d_{xz} are less well defined, since these are very dependent on the value of α, and could well be reversed (see Table 9). The extent of the $d_{x^2-y^2} - d_{z^2}$ mixing was determined from the crystal-field calculation which for $Dq = -1100$ cm^{-1} and $Cp = -5000$ cm^{-1} gave $(x^2 - y^2) = 0{\cdot}9988\ d_{x^2-y^2} - 0{\cdot}0512\ d_{z^2}$. These calculations again show that considerable care is required when interpreting magnetic parameters in terms of k values and MO coefficients.[9,12a]

TABLE 9

Calculated values of (*a*) β/γ_1 and (*b*) γ_1/γ_2

(*a*)	k_z/k_x \ α	0·6	0·7	0·8	0·9	1·0
$\delta = 1{\cdot}0$	1·00	0·93	0·96	0·98	0·99	1·00
	0·90	0·83	0·86	0·88	0·89	0·90
$\delta = 0{\cdot}90$	1·00	0·95	0·97	0·99	1·00	1·01
	0·90	0·86	0·87	0·89	0·90	0·91

(*b*)	k_z/k_y \ α	0·6	0·7	0·8	0·9	1·0
$\delta = 1{\cdot}0$	1·00	1·13	1·09	1·05	1·02	1·00
	0·90	1·02	0·98	0·95	0·92	0·90
	0·88	0·99	0·95	0·92	0·90	0·88
$\delta = 0{\cdot}90$	1·00	1·10	1·05	1·02	1·00	0·99
	0·90	0·99	0·95	0·92	0·90	0·89
	0·88	0·97	0·92	0·90	0·88	0·87

The changes in the molecular g values observed on cooling the system to 160 K are in the same sense as those observed for ammonium copper(II) sulphate hexahydrate.[19] The tendency towards axial symmetry, at the lower temperature, is more easily correlated with the axial Cu–N bonds becoming more nearly equal in length rather than with angular distortions of the structure, since the directions of the molecular g values are essentially the same at both temperatures.

The calculations involved in the *X*-ray analysis were performed at the Triangle Universities Computation Centre, North Carolina, and those for the crystal-field calculation at the University of Manchester. We thank the U.S. National Science Foundation for funds (to A. T. M.) towards the purchase of the diffractometer, and the S.R.C. for financial support (of C. D. G. and F. E. M.)

[4/1696 *Received*, 13*th August*, 1974]

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