Crystal and Molecular Structure, Electron Spin Resonance, and Electronic Spectrum of Tetrakis(imidazole)dinitratocopper(II)

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The structure of the title compound has been established by single-crystal *X*-ray analysis. Crystals are orthorhombic, space group $Pna2_1$, a = 13.85(1), b = 9.83(1), c = 13.39(1) Å, Z = 4. The structure was solved by the heavy-atom method and atomic parameters were refined by full-matrix least-squares calculations to R 0.043 for 1 394 statistically significant reflections from diffractometer measurements. The copper atom has a tetragonally distorted octahedral co-ordination in which four imidazole nitrogen atoms define the basal plane, mean Cu–N 2.011 Å, and unidentate nitrato-oxygen atoms occupy the axial sites, mean Cu–O 2.566 Å. The mean copper atom displacement from the nitrato-group planes is 0.80 Å. The imidazole N–H groups all participate in an extensive N–H ··· O hydrogen bonded network involving one of the nitrato-oxygen atoms. 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.

We recently reported [1] the crystal, molecular, and electronic structures of $[Cu(im)_6][NO_3]_2$ (im =imidazole). Although the detailed crystal and molecular structures of a number of tetrakis(imidazole)copper(II) complexes are known [2-5] there appear to be no detailed single-crystal studies of their electronic structures. We now therefore report the results of such a study on $[Cu(im)_4(NO_3)_2]$ and make a comparison with similar data for $[Cu(im)_6][NO_3]_2$.

EXPERIMENTAL

Preparation of Tetrakis(imidazole)dinitratocopper(II).—Purple crystals of $[Cu(im)_4(NO_3)_2]$ were grown by slow evaporation of an ethanolic solution of $Cu(NO_3)_2{\cdot}6H_2O$ and imidazole (1 : 4).

Crystal Data.—$C_{12}H_{16}CuN_{10}O_6$, M = 459.9, Orthorhombic, a = 13.85(1), b = 9.83(1), c = 13.39(1) Å, U = 1 823 Å^3, D_m = 1.67, Z = 4, D_c = 1.675, $F(000)$ = 940. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 13.1 cm^{-1}. Space group $Pna2_1$ (C_{2v}^9), or $Pnma$ (D_{2h}^{16}) with b and c axes interchanged, from systematic absences: $h0l$ when $h \neq 2n$, $0kl$ when $k + l \neq 2n$; shown to be the former by structure solution and refinement.

Crystallographic Measurements.—A crystal of dimensions *ca.* 0.3 × 0.3 × 0.4 mm was oriented on a glass fibre to rotate around the c axis. Preliminary cell dimensions and space-group information were obtained from Weissenberg (Cu-K_α radiation, λ = 1.542 Å) and precession photographs (Mo-K_α radiation). The crystal was then transferred to an Enraf-Nonius CAD 3 automated diffractometer (Zr-filtered Mo-K_α radiation, take-off angle 3°) and accurate cell parameters were evaluated from a least-squares treatment of the θ, χ, ϕ angles for 40 high-angle reflections. One octant of intensity data for all accessible reflections with $2\theta < 55°$ were recorded by the θ—2θ scanning technique described previously [6] with scan ranges of $(0.90 + 0.20 \tan\theta)°$. From these measurements, 1 394 reflections having $I > 2.0\sigma(I)$, where $\sigma^2(I)$ = (scan count + background count), were corrected for Lorentz and polarization effects and used in the structure solution and refinement. No allowance was made for the small effects of absorption.

Structure Analysis.—With four $Cu(im)_4(NO_3)_2$ units in space group $Pnma$ the complex must possess either $C_i(\bar{1})$ symmetry with the copper atoms lying on centres of symmetry at Wyckoff positions [7] $4a$ $(0,0,0;\ 0,\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2})$ or $4b$ $(0,0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,0;\ \frac{1}{2},\frac{1}{2},0)$, or it must have $C_s(m)$ symmetry with the copper atoms lying in the symmetry planes at positions $4c$ $(x,\frac{1}{4},z;\ \bar{x},\frac{3}{4},\bar{z};\ \frac{1}{2},\frac{3}{4},\frac{1}{2} + z;\ \frac{1}{2} + x,\frac{1}{4},\frac{1}{2} - z)$. Copper atom co-ordinates (x = 0.1243, y = 0.2500, z = 0.0000) derived from the three-dimensional Patterson map were clearly incompatible with the requirements of positions $4a$ and $4b$, and so these possibilities were eliminated from further consideration.

A copper-phased three-dimensional observed Fourier synthesis had the expected pseudosymmetry resulting in an electron-density distribution which showed an apparent co-ordination of the copper atom by four coplanar imidazole ligands lying in planes at $x = \frac{1}{8},\frac{3}{8},\frac{5}{8},\frac{7}{8}$. Such an arrangement is physically impossible, for it results in too short intramolecular ligand–ligand separations and thus space group $Pnma$ was eliminated and $Pna2_1$, with the b and c axes interchanged, was concluded to be the correct choice.

The pseudosymmetry was broken, with considerable difficulty, through the gradual refinement of the structure model. Inclusion of approximate co-ordinates for a pair of *trans*-related imidazole ligands along with the copper atom into a round of structure factor and Fourier calculations led to an electron-density distribution from which positions for the remaining non-hydrogen atoms could be obtained. The ligand orientation was such that it approximated $\bar{1}$ symmetry at the copper atom. Attempts to refine this model by several cycles of full-matrix least-squares calculations met with difficulty due to the ill-conditioned nature of the least-squares matrix. Although R decreased to 0.110, the refinement yielded unacceptable molecular dimensions which showed very large differences between chemically equivalent bond lengths and valency angles.

Refinement of the structure parameters to yield more acceptable values was attained by an alternative approach. Since the x co-ordinate of the copper atom lay very close to

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[5] G. Fransson and B. K. S. Lundberg, *Acta Chem. Scand.*, 1972, **26**, 3969.

[6] D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, 1974, 363.

[7] 'International Tables for *X*-Ray Crystallography,' vol. I, 3rd edn., Kynoch Press, Birmingham, 1969, p. 151.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and anisotropic temperature factor parameters * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	1 244.1(5)	64.3(7)	2 500(—)	28.4(2)	67.6(6)	31.4(3)	3.9(3)	−7.3(9)	−12.6(10)
N(A1)	1 251(5)	1 302(6)	3 695(5)	39(3)	64(5)	47(4)	−8(8)	−1(7)	8(8)
C(A2)	1 317(6)	2 621(6)	3 634(7)	59(5)	64(6)	53(5)	−74(9)	−9(9)	−2(9)
N(A3)	1 224(6)	3 136(6)	4 596(5)	59(4)	78(6)	33(3)	−5(9)	−8(8)	−12(8)
C(A4)	1 260(7)	2 070(9)	5 295(7)	70(6)	117(9)	47(5)	51(14)	1(11)	−12(13)
C(A5)	1 259(7)	923(9)	4 682(6)	60(5)	99(8)	29(4)	4(12)	−13(9)	8(9)
N(B1)	2 686(4)	−108(5)	2 601(5)	35(2)	79(5)	35(3)	7(6)	6(7)	18(9)
C(B2)	3 193(6)	−681(8)	3 347(7)	44(4)	110(8)	46(5)	−23(11)	−27(7)	33(10)
N(B3)	4 146(5)	−555(6)	3 147(6)	47(4)	57(5)	79(5)	20(8)	−25(7)	−5(10)
C(B4)	4 243(6)	48(7)	2 227(9)	28(3)	74(7)	124(11)	6(9)	14(8)	−13(14)
C(B5)	3 356(6)	343(9)	1 888(7)	37(4)	126(9)	61(6)	2(11)	17(8)	7 (12)
N(C1)	1 240(5)	−1 196(6)	1 311(4)	37(3)	96(6)	23(3)	−4(9)	−15(6)	−6(7)
C(C2)	1 313(5)	−2 547(7)	1 316(6)	30(3)	87(6)	41(4)	21(8)	−6(8)	33(9)
N(C3)	1 212(5)	−3 057(6)	425(6)	47(4)	70(6)	74(5)	3(9)	−9(9)	−52(9)
C(C4)	1 278(7)	−2 019(8)	−222(5)	55(5)	107(8)	20(4)	−2(13)	−12(8)	−5(9)
C(C5)	1 312(7)	−876(8)	326(7)	67(6)	73(6)	45(5)	7(12)	20(10)	6(10)
N(D1)	−202(4)	188(5)	2 415(5)	35(3)	72(5)	34(3)	5(6)	1(6)	−18(7)
C(D2)	−721(5)	932(9)	1 844(6)	32(4)	145(10)	35(4)	−8(10)	−9(7)	20(11)
N(D3)	−1 649(5)	812(8)	1 983(6)	38(4)	146(9)	59(5)	−6(10)	−19(7)	−10(11)
C(D4)	−1 758(5)	−175(8)	2 714(6)	33(3)	155(10)	39(5)	4(10)	16(6)	30(11)
C(D5)	−840(6)	−534(7)	2 983(5)	46(4)	89(7)	32(4)	9(9)	24(6)	49(9)
O(1)	1 016(5)	−2 071(6)	3 628(5)	74(4)	123(6)	75(4)	12(8)	13(7)	119(8)
N(2)	1 329(5)	−2 933(6)	4 205(5)	51(4)	65(5)	55(4)	−11(8)	3(7)	−7(8)
O(3)	1 050(5)	−4 139(7)	4 014(8)	66(5)	86(5)	142(7)	5(9)	−27(10)	−54(10)
O(4)	1 848(6)	−2 667(8)	4 895(6)	74(4)	189(9)	91(4)	−94(11)	−94(8)	68(11)
O(1′)	1 501(5)	2 156(6)	1 436(5)	72(4)	104(6)	55(4)	18(8)	10(7)	20(8)
N(2′)	1 210(4)	3 006(5)	843(4)	27(3)	70(5)	26(3)	4(7)	7(5)	18(6)
O(3′)	1 461(5)	4 211(6)	930(7)	73(5)	69(5)	114(7)	−15(9)	−33(10)	−8(10)
O(4′)	716(5)	2 675(8)	126(6)	70(4)	182(9)	52(4)	−65(11)	−49(8)	19(11)

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

0.1250, it was placed exactly at this value and held there during several least-squares refinement cycles. Moreover, the complex geometry was constrained to be centrosymmetric about the copper atom by introducing symmetry-equivalent positions ($\frac{1}{4} - x, \bar{y}, \frac{1}{2} - z$; $\frac{3}{4} + x, y, \bar{z}$; $\frac{1}{4} + x, \frac{1}{2} - y, \bar{z}$; $\frac{3}{4} - x, \frac{1}{2} + y, \frac{1}{2} - z$) into the structure-factor calculations, in addition to the four general positions of space group $Pna2_1$. Several rounds of least-squares calculations, first with isotropic then with anisotropic temperature factors, reduced R to 0.112. During these iterations the imidazole nitrogen atoms were distinguished from carbon atoms by their relatively smaller temperature factors when treated as carbon atoms and their identities were reinforced by the hydrogen-bond scheme (*vide infra*).

Idealized hydrogen-atom co-ordinates were computed, assuming that they were positioned radially at 1.05 Å from the imidazole carbon and nitrogen atoms, and it was verified that these coincided with regions of significant positive electron density in a difference-Fourier synthesis. Inclusion of fixed hydrogen-atom contributions, all with B 5.0 Å^2, followed by several further rounds of least-squares adjustment of the non-hydrogen atom parameters reduced R to 0.108. The copper atom was then moved off the special x co-ordinate position (its z co-ordinate was held fixed to define the origin of the space group) to its earlier refined value and the imposed extra symmetry constraints were relaxed. Several more cycles of least-squares calculations brought refinement to convergence at R 0.043. Final atomic positional and thermal parameters are in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21556 (10 pp., 1 microfiche).*

For all structure-factor calculations, neutral atom scattering factors for copper, carbon, nitrogen, and oxygen were taken from ref. 8, for hydrogen from ref. 9, and anomalous dispersion corrections for copper from ref. 10. In the least-squares interations, $\Sigma w\Delta^2$ was minimized and the weighting scheme used [$\sqrt{w} = 1$ for $|F_o| < 20.0$ and $\sqrt{w} = 20.0/|F_o|$ for $|F_o| > 20.0$] showed no systematic dependence of $\langle w\Delta^2\rangle$ when analyzed in ranges of $|F_o|$.

TABLE 2

Calculated fractional co-ordinates ($\times 10^3$) for hydrogen atoms, labelled according to their bonded carbon or nitrogen atom

Atom	x	y	z
H(A2)	139	317	295
H(A3)	121	417	477
H(A4)	127	214	614
H(A5)	127	−7	497
H(B2)	288	−113	400
H(B3)	472	−88	361
H(B4)	491	27	187
H(B5)	320	84	122
H(C2)	136	−312	195
H(C3)	114	−410	21
H(C4)	128	−208	−100
H(C5)	138	10	6
H(D2)	−44	160	135
H(D3)	−223	133	162
H(D4)	−242	−54	305
H(D5)	−66	−124	353

Electron Spin Resonance Spectra.—E.s.r. spectra were recorded in the crystallographic *ab*, *bc*, and *ac* planes at room temperature by methods outlined previously.[11] In

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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[10] Ref. 7, vol. III, 2nd edn., 1968, p. 215.

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TABLE 3

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

g Value	Set (1) c	Set (1) b	Set (1) a
2.046 ± 0.001	86° 35′	89° 58′	3° 00′
2.048 ± 0.002	40° 50′	49° 15′	87° 20′
2.230 ± 0.002	49° 21′	40° 44′	87° 44′
Molecular axes			
Cu–N(B1) (y)	85° 36′	83° 55′	7° 30′
Cu–N(A1) (x)	35° 18′	54° 42′	89° 30′
Cu–O(1) (z)	52° 37′	37° 56′	84° 32′

g Value	Set (2) c	Set (2) b	Set (2) a
2.040 ± 0.001	60° 42′	64° 48′	40° 27′
2.055 ± 0.001	54° 36′	60° 26′	49° 32′
2.230 ± 0.002	49° 20′	40° 42′	89° 42′

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

the *ab* and *ac* planes only a single line was observed at all orientations. However, in the *bc* plane two broad absorptions were observed, one from each of the magnetically inequivalent molecules in the unit cell. These two lines were only sufficiently separated for reliable measurement over the range of angle 30—70° from the *b* axis and only these, plus the lines at the axis positions, have been used in the subsequent analysis. No copper hyperfine splittings were observed at any orientation. Data were treated by the method of Schonland [12] to give the principal molecular g values and their orientations with respect to the crystal axes (see Table 3). Of the two alternative sets of g values given by this treatment, we have chosen the one with direction cosines corresponding closest to those calculated from the crystallographic data for the Cu–N and Cu–O directions.

Single-crystal Polarised Electronic Spectra.—Absorption spectra were recorded as outlined previously.[1] Suitable crystals were oriented to permit spectra to be recorded with the electric vector of the incident beam to be polarised parallel to each of the crystallographic axes. In the range 8—20 kK,* each spectrum consisted of a strong absorption band at 18.8, a shoulder at *ca.* 15.5, and a much weaker shoulder at *ca.* 12.5 kK; the relative intensities of the spectra varying as $c > b > a$ polarisation.

Crystal-field Calculations.—Molecular g values and d–d transition energies were calculated as described earlier,[1] assuming D_{2h} symmetry to be appropriate for the CuN_4O_2 chromophore.

RESULTS AND DISCUSSION

Crystal and Molecular Structure.—Figure 1 shows a view of the co-ordination geometry around the copper atom and the atom labelling of the asymmetric crystal unit. The crystals contain discrete monomeric $[Cu(im)_4(NO_3)_2]$ units bridged by N–H · · · O hydrogen bonds (*vide infra*). Interatomic distances and valency angles are listed in Table 4, displacements of selected atoms from various least-squares planes in Table 5.

The co-ordination at the copper is tetragonally distorted octahedral with the basal plane defined by four coplanar imidazole nitrogen atoms (ΔCu 0.02 Å), and the axial sites occupied by unidentate nitrato-oxygen atoms. The copper atom lies close to each of the co-ordinated imidazole ring planes but it is very significantly displaced (Δ0.86, 0.74 Å) from the nitrato-group planes (Table 5). The mean Cu–N distance [2.011(7) Å] agrees well with the corresponding mean equatorial lengths in a number of other octahedral Cu(II) complexes with either uni- or bi-dentate *N*-donor ligands,[5,9,13,14] and is only slightly shorter than the corresponding mean distance [1] in $[Cu(im)_6][NO_3]_2$ [2.031(2) Å]. Also in the normal range is the mean Cu–O length (2.566 Å) which is close to values for other mean distances at the axial nitrato-oxygen atoms [15] and at the axial sulphato-oxygen atoms in $[Cu(im)_4][SO_4]$ [2.574(4) Å].[5]

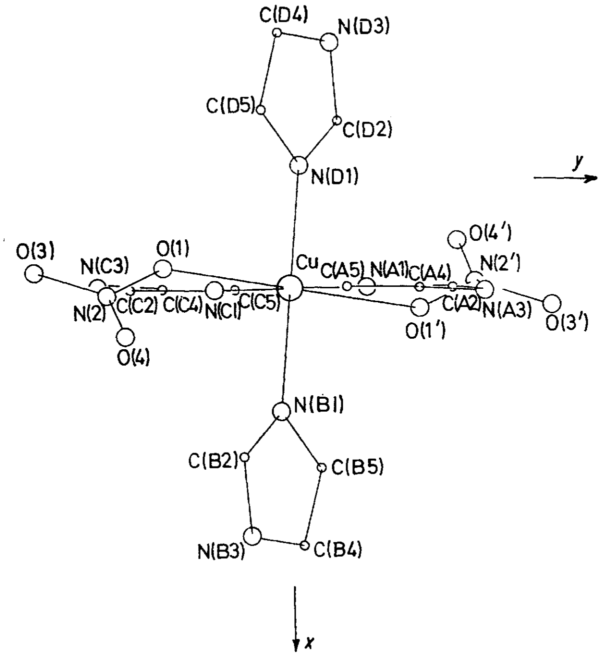

FIGURE 1 Copper atom co-ordination and atom numbering scheme

In the four imidazole rings there are apparently significant differences between chemically equivalent bonds as judged by the least-squares derived estimated standard deviations. However, deviations of the individual values from the mean should be viewed as an independent assessment of the standard deviations of the bond lengths involved rather than as genuine variations

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* 1 kK = 10^3 cm^{-1}.

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

[13] D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, in the press.

[14] A. F. Cameron, K. P. Forrest, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc.* (*A*), 1971, 2492.

[15] Y. Komiyama and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1145.

within the ligands, and they indicate that the least-squares values are too low. The mean bond lengths are in excellent agreement with the corresponding values found in free imidazole at −150 °C and with those reported for this neutral ligand in other complexes.[16,17] The orientations of the imidazole rings with respect to the CuN_4 equatorial plane vary between these different compounds. In $[Cu(im)_6][NO_3]_2$,[1] two imidazole rings are inclined at 70.1 and two at 35.6° to the CuN_4 plane, in $[Cu(im)_4][SO_4]$ [5] these angles are 99.0 and 29.7°, and in $[Cu(im)_4][ClO_4]_2$ they are 94.3 and 18.7°. In contrast to the rather different orientations of the pairs of imidazole rings in these three complexes, all the imidazole rings in $[Cu(im)_4(NO_3)_2]$ are very similarly orientated. The imidazole ring containing N(A1) is inclined at 94.6°, and that containing N(D1) at 98.6 °C, to the CuN_4 plane. Thus the nature of the π-bonding between the imidazole *N*-donor atoms and the copper 3*d* orbitals will vary within these compounds. The atomic arrangement adopted for $[Cu(im)_4(NO_3)_2]$ clearly maximises the $Cu(d_{xy})–N(p_\pi)$ overlap and minimises that involving the copper d_{xz} and d_{yz} orbitals.

Table 4

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

(*a*) Bond lengths

Cu–N(A1)	2.010(7)	N(C1)–C(C2)	1.332(9)
Cu–N(B1)	2.008(5)	N(C1)–C(C5)	1.359(11)
Cu–N(C1)	2.018(6)	C(C2)–N(C3)	1.302(11)
Cu–N(D1)	2.009(5)	N(C3)–C(C4)	1.341(10)
Cu–O(1)	2.606(6)	C(C4)–C(C5)	1.343(11)
Cu–O(1′)	2.526(6)	N(D1)–C(D2)	1.280(10)
N(A1)–C(A2)	1.302(8)	N(D1)–C(D5)	1.365(9)
N(A1)–C(A5)	1.373(11)	C(D2)–N(D3)	1.304(10)
C(A2)–N(A3)	1.390(11)	N(D3)–C(D4)	1.386(11)
N(A3)–C(A4)	1.406(11)	C(D4)–C(D5)	1.367(11)
C(A4)–C(A5)	1.395(12)	N(2)–O(1)	1.226(9)
N(B1)–C(B2)	1.345(10)	N(2)–O(3)	1.199(11)
N(B1)–C(B5)	1.403(11)	N(2)–O(4)	1.273(9)
C(B2)–N(B3)	1.353(10)	N(2′)–O(1′)	1.222(8)
N(B3)–C(B4)	1.373(13)	N(2′)–O(3′)	1.222(9)
C(B4)–C(B5)	1.341(12)	N(2′)–O(4′)	1.240(8)

(*b*) Valency angles

N(A1)–Cu–N(B1)	89.6(3)	C(B2)–N(B3)–C(B4)	108.2(7)
N(A1)–Cu–N(C1)	179.4(2)	N(B3)–C(B4)–C(B5)	107.9(8)
N(A1)–Cu–N(D1)	90.8(2)	N(B1)–C(B5)–C(B4)	107.9(8)
N(A1)–Cu–O(1)	91.5(2)	Cu–N(C1)–C(C2)	127.4(5)
N(A1)–Cu–O(1′)	87.5(2)	Cu–N(C1)–C(C5)	128.5(5)
N(B1)–Cu–N(C1)	90.2(3)	C(C2)–N(C1)–C(C5)	103.4(6)
N(B1)–Cu–N(D1)	178.5(2)	N(C1)–C(C2)–N(C3)	111.8(6)
N(B1)–Cu–O(1)	90.8(2)	C(C2)–N(C3)–C(C4)	106.9(6)
N(B1)–Cu–O(1′)	88.1(2)	N(C3)–C(C4)–C(C5)	106.7(7)
N(C1)–Cu–N(D1)	89.4(2)	N(C1)–C(C5)–C(C4)	109.5(7)
N(C1)–Cu–O(1)	87.9(2)	Cu–N(D1)–C(D2)	128.9(5)
N(C1)–Cu–O(1′)	93.1(2)	Cu–N(D1)–C(D5)	125.6(5)
N(D1)–Cu–O(1)	87.8(2)	C(D2)–N(D1)–C(D5)	105.4(6)
N(D1)–Cu–O(1′)	93.4(2)	N(D1)–C(D2)–N(D3)	114.6(7)
O(1)–Cu–O(1′)	178.5(2)	C(D2)–N(D3)–C(D4)	105.8(7)
Cu–N(A1)–C(A2)	123.6(6)	N(D3)–C(D4)–C(D5)	105.4(6)
Cu–N(A1)–C(A5)	127.0(5)	N(D1)–C(D5)–C(D4)	108.7(6)
C(A2)–N(A1)–C(A5)	109.2(7)	Cu–O(1)–N(2)	151.6(5)
N(A1)–C(A2)–N(A3)	107.4(7)	O(1)–N(2)–O(3)	114.2(7)
C(A2)–N(A3)–C(A4)	110.0(6)	O(1)–N(2)–O(4)	123.2(7)
N(A3)–C(A4)–C(A5)	102.1(8)	O(3)–N(2)–O(4)	122.7(8)
N(A1)–C(A5)–C(A4)	110.3(7)	Cu–O(1′)–N(2′)	151.2(5)
Cu–N(B1)–C(B2)	127.2(5)	O(1′)–N(2′)–O(3′)	119.9(6)
Cu–N(B1)–C(B5)	125.9(5)	O(1′)–N(2′)–O(4′)	120.9(6)
C(B2)–N(B1)–C(B5)	107.0(6)	O(3′)–N(2′)–O(4′)	119.1(7)
N(B1)–C(B2)–N(B3)	108.9(7)		

(*c*) Intermolecular separations $\leqslant 3.5$ Å

$O(3')\cdots N(A3^{II})$	2.79	$C(A2)\cdots O(3^{II})$	3.25
$N(A3)\cdots O(3^{II})$	2.80	$N(D3)\cdots O(1'^{III})$	3.33
$N(B3)\cdots O(3^{IV})$	2.90	$O(1')\cdots N(4'^{VI})$	3.33
$N(D3)\cdots O(3'^{III})$	2.97	$O(4)\cdots N(D3^{I})$	3.35
$N(2)\cdots O(4'^{I})$	3.10	$N(A3)\cdots C(C4^{V})$	3.47
$O(1)\cdots O(4'^{I})$	3.18	$O(4)\cdots C(D2^{I})$	3.49
$O(3)\cdots O(4'^{I})$	3.21	$C(D5)\cdots C(C5^{I})$	3.49
$O(3')\cdots C(A2^{II})$	3.24	$C(A5)\cdots C(D2^{I})$	3.50

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

I	$-x, -y, \tfrac{1}{2} + z$	IV	$\tfrac{1}{2} + x, -\tfrac{1}{2} - y, z$
II	$x, 1 + y, z$	V	$\tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} + z$
III	$-\tfrac{1}{2} + x, \tfrac{1}{2} - y, z$	VI	$\tfrac{1}{2} + x, \tfrac{1}{2} - y, z$

At the axial nitrato-groups the Cu–O distances exhibit small, but genuine, differences probably due to crystal packing effects related to the hydrogen bonding described later. The mean Cu–O distances (2.57, 4.21, and 4.60 Å) show clearly the unidentate nature of these ligands in the present complex. The non-bonded intramolecular interactions with the imidazole ligands

Table 5

Equations of least-squares planes in the form $AX + BY + CZ + D = 0$, where X,Y,Z are in Å, and in square brackets displacements (Å) of relevant atoms from the planes

Plane (*A*): N(A1), C(A2), N(A3), C(A4), C(A5)

$$-0.9997X + 0.0007Y - 0.0230Z + 1.8815 =$$

[N(A1) 0.04, C(A2) −0.05, N(A3) 0.05, C(A4) −0.03, C(A5) −0.01, Cu 0.08]

Plane (*B*): N(B1), C(B2), N(B3), C(B4), C(B5)

$$-0.0328X - 0.8904Y - 0.4539Z + 1.5989 = 0$$

[N(B1) −0.01, C(B2) 0.02, N(B3) −0.02, C(B4) 0.01, C(B5) 0.00, Cu −0.03]

Plane (*C*): N(C1), C(C2), N(C3), C(C4), C(C5)

$$-0.9997X + 0.0258Y + 0.0007Z + 1.8085 = 0$$

[N(C1) 0.06, C(C2) −0.07, N(C3) 0.05, C(C4) −0.01, C(C5) −0.03, Cu 0.09]

Plane (*D*): N(D1), C(D2), N(D3), C(D4), C(D5)

$$-0.0162X - 0.7205Y - 0.6932Z + 2.3664 = 0$$

[N(D1) 0.00, C(D2) 0.01, N(D3) −0.01, C(D4) 0.01, C(D5) −0.01, Cu −0.03]

Plane (*E*): O(1), N(2), O(3), O(4)

$$0.7986X - 0.1308Y - 0.5875Z + 1.4629 = 0$$

[O(1) 0.00, N(2) 0.00, O(3) 0.00, O(4) 0.00, Cu 0.86]

Plane (*F*): O(1′), N(2′), O(3′), O(4′)

$$0.8167X - 0.1632Y - 0.5536Z - 0.2813 = 0$$

[O(1′) 0.01, N(2′) −0.02, O(3′) 0.01, O(4′) 0.01, Cu −0.74]

Plane (*G*): N(A1), N(B1), N(C1), N(D1)

$$0.0952X + 0.7889Y - 0.6071Z + 1.8368 = 0$$

[N(A1) 0.01, N(B1) −0.01, N(C1) 0.01, N(D1) −0.01, Cu 0.02, O(1) −2.59, O(1′) 2.54]

Dihedral angles (°) between the plane normals:

(*A*)–(*B*)	88	(*B*)–(*D*)	17	(*C*)–(*G*)	94
(*A*)–(*C*)	2	(*B*)–(*E*)	69	(*D*)–(*E*)	61
(*A*)–(*D*)	88	(*B*)–(*F*)	68	(*D*)–(*F*)	61
(*A*)–(*E*)	142	(*B*)–(*G*)	155	(*D*)–(*G*)	99
(*A*)–(*F*)	144	(*C*)–(*D*)	90	(*E*)–(*F*)	3
(*A*)–(*G*)	95	(*C*)–(*E*)	143	(*E*)–(*G*)	71
(*B*)–(*C*)	89	(*C*)–(*F*)	145	(*F*)–(*G*)	73

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[17] K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, 1972, **94**, 727.

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appear to prevent the close approach of the nitrato-oxygen atoms 4 and 4′ to the metal. Thus these Cu · · · O separations (4.21 Å) and the Cu–O(1)–N angles (151.4°) are larger than usually found for unidentate nitrato-groups.[18] The mean N–O bond length obtained here [1.230(25) Å] is not significantly different from the mean of means [1.245(10) Å] from several recent accurate structural determinations.[1,18-22] Individual N–O distances and O–N–O interbond angles from the present study are not determined with sufficient accuracy (*vide supra*) to reveal any systematic small variations which may be dependent upon the extent of the co-ordination with the metal atom and which are recognised to be present in a number of nitrato-complexes.[18] The highly significant displacement of the copper atom from the nitrato-planes is unusual, the normal co-ordination geometry being that in which the metal atom lies in or close to the nitrato-group plane, but it does resemble the tilt at the axial imidazole in $[Cu(im)_6][NO_3]_2$.[1] The mean Cu–O–N angle [151.4(5)°] is also strikingly similar to the Cu–N–M (where M is the centroid of the imidazole ring) angle (150.4°) at the axial imidazole ligands in $[Cu(im)_6][NO_3]_2$ and to the Cu–O–S angle (152.4°) at the unidentate axial sulphato-groups in $[Cu(im)_4][SO_4]$.[5] Thus the angle subtended at the axial ligand remains approximately constant despite the considerably different packing arrangements in crystals of these three complexes each of which has an extensive hydrogen-bonding network, suggesting that this may be determined by intramolecular interactions between the axial ligand and an equatorial imidazole group whose plane is *ca.* perpendicular to the CuN_4 plane.

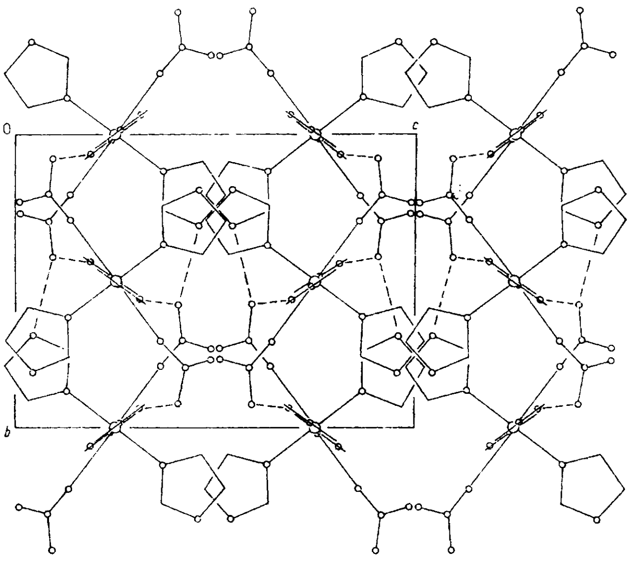

FIGURE 2 Crystal packing arrangement, viewed in projection along the *a* axis; N–H · · · O hydrogen bonds are denoted by broken lines

Figure 2 shows a view of the crystal packing. The shorter intermolecular separations of Table 4 occur between imidazole nitrogen atoms and nitrato-oxygen atoms. Although these are typical for N–H · · · O hydrogen-bonding interactions the inequality of the pairs of C–N · · · O angles (151.7, 97.8; 154.3, 95.7; 143.2, 103.5; 143.1, 108.4°) clearly indicate that the hydrogen atoms involved do not lie along the N · · · O line of centres. The other distances quoted correspond to normal van der Waals interactions.

TABLE 6

Assignment of the electronic spectra of $[Cu(im)_4(NO_3)_2]$ and $[Cu(im)_6][NO_3]_2$

Transition	Assignment of experimental band maxima/kK *			
	$[Cu(im)_4(NO_3)_2]$		$[Cu(im)_6][NO_3]_2$	
	A	*B*	*A*	*B*
$x^2 - y^2 \rightarrow xy$	12.5	15.4	12.5	10.7
$x^2 - y^2 \rightarrow z^2$	15.4	12.5	10.7	12.5
$x^2 - y^2 \rightarrow xz$ yz	18.8	18.8	16.2	16.2

* 1 kK = 10^3 cm^{-1}.

Electronic Structure.—Assuming that the gross symmetry of the CuN_4O_2 arrangement will be the most important factor in determining the electronic structure of the chromophore, we have interpreted our data on the basis of the D_{2h} point-group rather than on the actual lower symmetry of the molecule. Because the molecules are not all oriented in the same manner in the crystal, and all the *d–d* transitions are electronically forbidden but most are vibronically allowed, an unambiguous assignment of the spectrum is difficult. The two most probable assignments of the electronic spectra of $[Cu(im)_4(NO_3)_2]$ and $[Cu(im)_6][NO_3]_2$ are given in Table 6. In view of the very similar equatorial Cu–N bond lengths it would be expected that the energy separation between the copper $d_{x^2-y^2}$ and d_{xy} orbitals in these two systems would also be similar. This expectation indicates that the assignment *A* for each of these compounds is the most likely. This differs from that previously suggested for $[Cu(im)_6][NO_3]_2$.[1] The increase in the energy of the $x^2 - y^2 \rightarrow z^2$ transition from $[Cu(im)_6][NO_3]_2$ to $[Cu(im)_4(NO_3)_2]$ may be seen as a consequence of replacing the axial *N*- by *O*-donor ligands.

These assignments of the *d–d* transition energies and molecular *g* values for both $[Cu(im)_6][NO_3]_2$ and $[Cu(im)_4(NO_3)_2]$ have been interpreted on the basis of a modified crystal-field model.[1] For the former, the new assignment of the spectrum can be satisfactorily accounted for assuming Dq —1 300 and Cp —400 cm^{-1} (these parameters refer to Cu–N 2.012 Å, Table 8 of ref. 1). The values of the orbital-reduction parameters required to reproduce the molecular *g* values are then slightly changed from those given earlier,[1] the ranges now being k_z 0.73—0.74, k_x 0.72—0.78, and k_y 0.76—0.80. However, these new parameters do not alter the previously reported[1]

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

[21] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1972, 1608.

[22] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1973, 2130.

relative magnitudes of the MO coefficients, α, β, δ, γ_1, and γ_2 of the copper $d_{x^2-y^2}$, d_{xy}, d_{z^2}, d_{yz}, and d_{xz} orbitals in the antibonding molecular orbitals, namely $\beta < \gamma_1 \leqslant \gamma_2$. A similar crystal-field approach for $[Cu(im)_4(NO_3)_2]$ gave a reasonable interpretation of the spectral data, with $x^2 - y^2 \rightarrow xy, \rightarrow z^2, \rightarrow xz, yz$ being calculated at 12.6, 14.4, and 19.2 kK, respectively, using Dq −1 250 and Cp −4 000 cm^{-1} for Cu–N 2.012 Å, these parameters being suitably scaled according to the actual metal–ligand separations (R),[23] and Dq −400 and Cp −1 000 cm for Cu–O 2.566 Å. These crystal-field parameters were used to find values of the orbital-reduction parameters which would give calculated molecular g values in agreement with experiment. The range of values thus calculated was k_z 0.66—0.68 and $k_x = k_y = 0.74$—0.82.

The interpretation of these latter orbital-reduction parameters in terms of MO coefficients is much simpler than in the case of $[Cu(im)_6][NO_3]_2$. The crystal-field for $[Cu(im)_4(NO_3)_2]$ causes negligible mixing between the $d_{x^2-y^2}$ and d_{z^2} orbitals $[(x^2 - y^2) = 1.0000\ d_{x^2-y^2} + 0.0064\ d_{z^2}]$, and hence it is a good approximation to write: $k_z = \alpha\beta$, $k_x = \alpha\gamma_1$, and $k_y = \alpha\gamma_2$. The relative magnitudes of the calculated orbital-reduction factors thus give $\beta < \gamma_1 = \gamma_2$. This sequence is consistent with the orientations of the imidazole rings in $[Cu(im)_4(NO_3)_2]$ which allow for significant overlaps between the π orbitals of the imidazole rings and the copper d_{xy} orbital, but negligible such overlap with the copper d_{xz} and d_{yz} orbitals.

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