Crystal Structure and Properties of Bis(benzimidazol-2-ylmethanol-*N'O*)(nitrato-*NO*)copper(II) Nitrate Monohydrate

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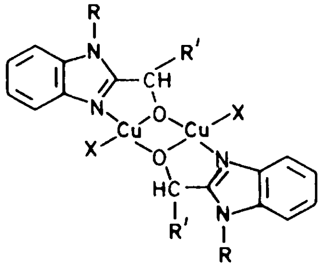
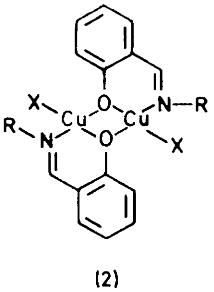
The crystal and molecular structures of the title complex, $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$, have been determined by single-crystal *X*-ray diffraction using counter methods. Crystal data: space group $P\bar{1}$, $a = 8.562(4)$, $b = 9.990(4)$, $c = 13.546(1)$ Å, $\alpha = 90.16(2)$, $\beta = 100.86(2)$, $\gamma = 118.29(4)°$, and $Z = 2$. Refinement carried out by full-matrix least squares has reached a conventional R factor of 0.025. The ligand environment of the copper atom corresponds approximately to a tetragonally distorted octahedron. The two Hbim ligands are bidentate, bonding *via* one of the nitrogen atoms and the methanol oxygen. A co-ordinated bidentate nitrate group completes the octahedron. Hydrogen-bonding interactions between the other, unco-ordinated, nitrate group, the water of crystallisation, and the $[Cu(Hbim)_2(NO_3)]^+$ cations form an extensively linked polymeric network. High-precision magnetic-susceptibility measurements show that the polymeric structure is strictly magnetically dilute down to liquid-helium temperatures. This contrasts with literature data that imply slight antiferromagnetic interactions in this complex and three of its structural analogues.

BENZIMIDAZOLE substituted at the 2-position by α- or β-hydroxyalkyl groups forms a potential bidentate and binucleating ligand. Binuclear complexes of copper(II) with such ligands have been synthesised and the structure (1) has been proposed on the basis of their magnetic behaviour.[1] An analogous binuclear structure (2), proposed on the basis of magnetic behaviour,[2] has been confirmed by crystal structures.[3]



(1)
X = Br or Cl



(2)
X = alkyl or aryl

Unlike the salicylaldimine ligands in (2) the benzimidazole ligands can readily co-ordinate *via* the alkanol hydroxyl group, either deprotonated or intact. If not deprotonated, this hydroxyl oxygen is much less electronegative, and is therefore less likely to bond to two metal atoms simultaneously to form the bridge in a binuclear complex, especially if sufficient other donor atoms are available to satisfy the co-ordination sphere of the metal atom. We describe here the synthesis and structure of a complex of undeprotonated benzimidazol-2-ylmethanol (Hbim) with copper(II) nitrate.

EXPERIMENTAL

The ligand was prepared as previously described from *o*-phenylenediamine and hydroxyacetic acid.[1,4,5] The complex was prepared by combining, in a 1 : 2 mol ratio, a water–ethanol (1 : 1) solution of copper(II) nitrate with an ethanol solution of the ligand. The complex formed as green crystals, one of which was suitable for the *X*-ray study (Found: C, 38.5; H, 3.5; Cu, 13.4. $C_{16}H_{18}CuN_6O_9$ requires C, 38.4; H, 3.6; Cu, 12.7%).

Magnetic susceptibilities and moments were determined using a superconducting susceptometer incorporating a Josephson junction magnetometer, superconducting magnets, and shields.[6] Infrared spectra were recorded on a model no. 301 Perkin-Elmer instrument with a 6X beam condenser, using a diamond-anvil cell.[7] The instrument was calibrated in the far-i.r. region with water vapour, red HgO, and Hg emission lines.

Crystal Data for $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$.—$C_{16}H_{18}CuN_6O_9$, $M = 502$, space group $P\bar{1}$, $a = 8.562(4)$, $b = 9.990(4)$, $c = 13.546(1)$ Å, $\alpha = 90.16(2)$, $\beta = 100.86(2)$, $\gamma = 118.29(4)°$, $U = 996$ Å^3, λ (Mo-K_α) = 0.7017 Å, μ(Mo-K_α) = 12.1 cm^{-1}, $D_m = 1.70$ g cm^{-3}, $Z = 2$, $D_c = 1.67$ g cm^{-3}, crystal dimensions (mm of faces from centroid): $(2\bar{1}0)$ 0.26, $(\bar{2}10)$ 0.26, (011) 0.24, $(0\bar{1}\bar{1})$ 0.24, $(01\bar{1})$ 0.25, $(0\bar{1}1)$ 0.25.

The Enraf–Nonius program SEARCH was used to produce 25 accurately centred reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 28 accurately centred reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the X-*Ray Data*.—Diffraction data were collected at 292 K on an Enraf–Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo-K_α radiation from a highly orientated graphite crystal monochromator. The θ—2θ scan technique was used to record the intensities for all non-equivalent reflections for which $0 > 2\theta > 46°$. Scan widths (SW) were calculated from the formula $SW = A + B\tan\theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in widths of peaks due to $K_{\alpha 1} - K_{\alpha 2}$ splitting. The values of A and B were 0.6 and 0.35° respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2), where TOT is the integrated peak intensity.

The intensities of three standard reflections, monitored at

100-min intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarisation effects (including the polarisation effect of the crystal monochromator) and then for absorption. After averaging of the intensities of equivalent reflections, the data were reduced to 2 437 independent intensities of which 2 350 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[8] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure.—The positions of the metal and of five of the six ligand donor atoms were obtained from a three-dimensional Patterson synthesis calculated from all the intensity data. The positions of the remaining non-hydrogen atoms were determined from a Fourier-difference function. One of the two $[NO_3]^-$ groups was found to be co-ordinated as a bidentate ligand, and the other a free anion in the lattice. The anionic $[NO_3]^-$ group was positionally disordered in two main positions, related by a rotation about the N atom.

Full-matrix least-squares refinement was based on F, and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure-factor amplitudes. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber,[9] and those for hydrogen from Stewart *et al.*[10] The effects of anomalous dispersion for all the non-hydrogen atoms were included in F_c using the values of Cromer and Ibers [11] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. The principal programs used have been described.[12]

The occupancies of the two $[NO_3]^-$ positions were refined and comparison of the thermal parameters indicated values of 0.67 and 0.33. Anisotropic temperature factors were introduced for the copper and ligand oxygen atoms and further refinement was carried out. A Fourier-difference function now located all the hydrogen atoms of the Hbim ligands. Anisotropic temperature factors were included for all the non-hydrogen atoms, and full-matrix least squares was carried out on all parameters including those for the hydrogen atoms. The hydrogen-atom positions for the water molecule included in the lattice were then determined from a Fourier-difference function. The hydrogen atoms were included in the refinement for three cycles and subsequently held fixed. The occupancy of the two disordered positions of the anionic $[NO_3]^-$ group was refined both with anisotropic and isotropic thermal parameters, and confirmed to be in the ratio 2 : 1. The model converged with $R = 0.025$, $R' = 0.026$. The largest parameter shift at convergence was less than one tenth of its estimated standard deviation. A parallel calculation of the structure solution in space group $P\bar{1}$ produced the same result with the nitrate disorder persisting, but without a statistically significant improvement of the correlation in either of the possible absolute configurations.[13] Thus, the acentric model was rejected and space group $P\bar{1}$ was chosen. A structure-factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 0.027$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier-difference function was featureless. Tables of thermal parameters, details of least-squares planes, and the observed structure factors are available as Supplementary Publication No. SUP 22401 (15 pp.).*

RESULTS AND DISCUSSION

Final positional parameters are given in Table 1, bond lengths and angles in Tables 2 and 3. The digits in parentheses in the Tables are the estimated standard deviations in the least-significant figures quoted and were derived from the inverse matrix in the course of the least-squares refinement. Figure 1 is a stereoscopic pair of $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$ while Figure 2 shows the molecular packing in the unit cell.

TABLE 1

Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*
Cu	0.041 36(4)	0.200 37(3)	0.217 12(2)
O(A)	−0.193 6(2)	0.050 2(2)	0.121 1(1)
O(B)	0.003 2(2)	0.375 3(2)	0.303 6(1)
O(1C)	0.308 0(2)	0.297 1(2)	0.289 1(1)
O(2C)	0.247 3(2)	0.095 4(2)	0.197 5(1)
O(3C)	0.520 3(2)	0.239 6(2)	0.284 7(2)
O(1D)	−0.337 9(5)	0.089 1(4)	−0.371 4(3)
O(2D)	−0.209 9(5)	0.323 0(4)	−0.415 9(3)
O(3D)	−0.235 2(5)	0.303 7(4)	−0.272 4(2)
O(1E)	0.255 2(5)	0.719 3(4)	0.248 0(2)
O(2E)	−0.352 7(5)	0.109 6(4)	−0.376 2(3)
O(3E)	−0.183 2(6)	0.327 8(4)	−0.405 7(3)
O	−0.481 0(2)	−0.026 2(2)	0.187 2(1)
N(1A)	0.080 6(2)	0.299 7(2)	0.093 4(1)
N(1B)	−0.057 4(2)	0.093 2(2)	0.329 0(1)
N(3A)	−0.023 0(2)	0.310 0(2)	−0.066 5(1)
N(3B)	−0.205 2(2)	0.061 7(2)	0.450 5(1)
N(C)	0.361 3(3)	0.210 1(2)	0.257 2(2)
N(D)	−0.262 7(3)	0.237 6(2)	−0.348 9(2)
C(2A)	−0.055 5(3)	0.232 1(3)	0.014 4(2)
C(4A)	0.146 3(3)	0.438 3(3)	−0.039 2(2)
C(5A)	0.211 6(3)	0.430 7(2)	0.062 0(2)
C(6A)	0.381 2(3)	0.542 4(3)	0.113 2(2)
C(7A)	0.481 4(3)	0.658 1(3)	0.060 4(2)
C(8A)	0.414 3(3)	0.664 5(3)	−0.040 4(2)
C(9A)	0.246 7(3)	0.556 9(3)	−0.092 0(2)
C(10A)	−0.219 5(3)	0.087 8(3)	0.020 1(2)
C(2B)	−0.105 3(3)	0.160 7(3)	0.392 1(2)
C(4B)	−0.227 4(3)	−0.079 7(3)	0.424 5(2)
C(5B)	−0.133 1(3)	−0.059 6(3)	0.347 6(2)
C(6B)	−0.129 9(3)	−0.182 4(3)	0.312 4(2)
C(7B)	−0.224 0(4)	−0.322 8(3)	0.335 6(2)
C(8B)	−0.319 0(4)	−0.341 7(3)	0.411 6(2)
C(9B)	−0.320 9(4)	−0.221 6(3)	0.457 8(2)
C(10B)	−0.057 6(3)	0.324 0(3)	0.394 3(2)
H(1A)	−0.276(3)	0.033(3)	0.140(2)
H(1B)	0.076(4)	0.458(3)	0.311(2)
H(01)	−0.536(5)	−0.105(4)	0.208(3)
H(02)	−0.466(4)	0.033(3)	0.218(2)
H(3A)	−0.091(3)	0.289(3)	−0.115(2)
H(6A)	0.427(3)	0.540(3)	0.184(2)
H(7A)	0.594(3)	0.731(3)	0.091(2)
H(8A)	0.488(3)	0.744(3)	−0.068(2)
H(9A)	0.195(3)	0.559(3)	−0.157(2)
H(101A)	−0.336(3)	0.084(3)	−0.002(2)
H(102A)	−0.232(3)	0.006(3)	−0.025(2)
H(3B)	−0.247(3)	0.084(2)	0.484(2)
H(6B)	−0.063(3)	−0.170(3)	0.252(2)
H(7B)	−0.221(3)	−0.410(3)	0.307(2)
H(8B)	−0.382(4)	−0.439(3)	0.429(2)
H(9B)	−0.380(4)	−0.231(3)	0.500(2)
H(101B)	−0.173(3)	0.335(3)	0.395(2)
H(102B)	0.048(4)	0.386(3)	0.453(2)

The complex consists of monomeric complex cations $[Cu(Hbim)_2(NO_3)]^+$, well separated from one another,

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

anionic nitrate groups, and waters of crystallisation, all of which are involved in hydrogen bonding with each other. The $[NO_3]^-$ anion is disordered about two positions with a 2 : 1 occupancy ratio, and related by a rotation of *ca.* 12° about the nitrogen atom. In both positions the $[NO_3]^-$ group is involved in simultaneous hydrogen bonding with adjacent cations, *via* hydrogen atoms on oxygen or nitrogen ligand atoms, and with the water of crystallisation. The water molecule is hydrogen-bonded not only to the anionic $[NO_3]^-$ group but also to one of the Hbim ligands *via* the hydrogen atom of the alcoholic oxygen. These hydrogen-bonding interactions form an infinite polymeric network.

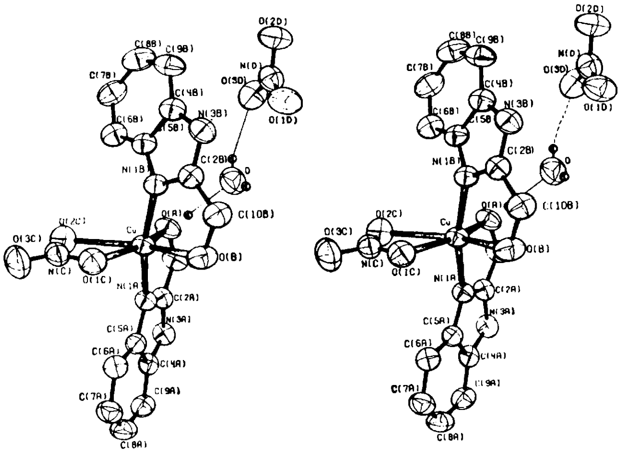

FIGURE 1 Stereopair of $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$

TABLE 2

Bond lengths (Å) for $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$

Cu–O(A)	2.045(1)	N(D)–O(1D)	1.32(1)
Cu–O(B)	2.285(1)	N(D)–O(2D)	1.247(5)
Cu–O(1C)	2.055(1)	N(D)–O(3D)	1.151(5)
Cu–O(2C)	2.501(1)	N(D)–O(2E)	1.15(1)
Cu–N(1A)	1.955(1)	N(D)–O(3E)	1.221(6)
Cu–N(1B)	1.949(1)	C(2A)–C(10A)	1.484(1)
O(A)–C(10A)	1.426(1)	C(4A)–C(5A)	1.399(1)
O(B)–C(10B)	1.427(1)	C(4A)–C(9A)	1.390(1)
O(1C)–N(C)	1.266(1)	C(5A)–C(6A)	1.393(1)
O(2C)–N(C)	1.253(1)	C(6A)–C(7A)	1.374(1)
O(3C)–N(C)	1.237(1)	C(7A)–C(8A)	1.396(1)
N(1A)–C(2A)	1.326(1)	C(8A)–C(9A)	1.372(1)
N(1A)–C(5A)	1.399(1)	C(2B)–C(10B)	1.484(1)
N(1B)–C(2B)	1.323(1)	C(4B)–C(5B)	1.395(1)
N(1B)–C(5B)	1.397(1)	C(4B)–C(9B)	1.388(1)
N(3A)–C(2A)	1.342(1)	C(5B)–C(6B)	1.385(1)
N(3A)–C(4A)	1.392(1)	C(6B)–C(7B)	1.377(1)
N(3B)–C(2B)	1.341(1)	C(7B)–C(8B)	1.390(1)
N(3B)–C(4B)	1.371(1)	C(8B)–C(9B)	1.363(1)

Hydrogen-bonding interactions

Atom 1	H atom	Atom 2	*D* [a]	*d* [b]	Angle (°)
O(A)	H(1A)	O	2.56 [c]	1.82	175
O(B)	H(1B)	O(3E)	2.83 [d]	2.18	143
O(B)	H(1B)	O(2D)	2.92 [d]	2.27	144
O(B)	H(1B)	O(3D)	2.97 [d]	2.24	158
O(3C)	H(02)	O	2.96 [e]	2.32	163
O(1D)	H(3B)	N(3B)	2.92 [f]	2.26	155
O(3D)	H(01)	O	3.12 [g]	2.36	160
O(1E)	H(01)	O	2.76 [h]	2.00	159
O(2E)	H(3B)	N(3B)	3.01 [f]	2.32	162

[a] Atom 1 to atom 2. [b] H atom to atom 2. [c] Symmetry x, y, z. [d] Symmetry $-x, 1 - y, -z$. [e] Symmetry $1 + x, y, z$. [f] Symmetry $x, y, z - 1$. [g] Symmetry $1 - x, -y, -z$. [h] Symmetry $x - 1, y - 1, z$.

TABLE 3

Bond angles (°) for $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$

O(A)–Cu–O(B)	111.0(2)	O(2D)–N(D)–O(3D)	113(4)
O(A)–Cu–O(1C)	157.6(3)	O(2D)–N(D)–O(2E)	116(6)
O(A)–Cu–O(2C)	102.3(2)	O(2D)–N(D)–O(3E)	11(7)
O(A)–Cu–N(1A)	80.7(2)	O(3D)–N(D)–O(2E)	130(5)
O(A)–Cu–N(1B)	88.6(2)	O(3D)–N(D)–O3E)	109(4)
O(B)–Cu–O(1C)	91.4(3)	O(2E)–N(D)–O(3E)	121(5)
O(B)–Cu–O(2C)	146.4(2)	N(1A)–C(2A)–N(3A)	111.6(7)
O(B)–Cu–N(1A)	98.1(2)	N(1A)–C(2A)–C(10A)	121.6(7)
O(B)–Cu–N(1B)	77.2(2)	N(3A)–C(2A)–C(10A)	126.8(8)
O(1C)–Cu–O(2C)	55.3(2)	N(3A)–C(4A)–C(5A)	105.7(7)
O(1C)–Cu–N(1A)	96.8(3)	N(3A)–C(4A)–C(9A)	132.7(8)
O(1C)–Cu–N(1B)	96.5(2)	C(5A)–C(4A)–C(9A)	121.6(8)
O(2C)–Cu–N(1A)	91.2(2)	N(1A)–C(5A)–C(4A)	108.0(7)
O(2C)–Cu–N(1B)	100.0(3)	N(1A)–C(5A)–C(6A)	131.3(8)
N(1A)–Cu–N(1B)	166.0(3)	C(4A)–C(5A)–C(6A)	120.7(8)
Cu–O(A)–C(10A)	116.4(3)	C(5A)–C(6A)–C(7A)	117.6(8)
Cu–O(B)–C(10B)	112.0(4)	C(6A)–C(7A)–C(8A)	121.1(9)
Cu–O(1C)–N(C)	104.0(6)	C(7A)–C(8A)–C(9A)	122.3(8)
Cu–O(2C)–N(C)	83.3(5)	C(4A)–C(9A)–C(8A)	116.7(8)
Cu–N(1A)–C(2A)	114.8(6)	O(A)–C(10A)–C(2A)	106.4(7)
Cu–N(1A)–C(5A)	133.3(6)	N(1B)–C(2B)–N(3B)	111.2(8)
C(2A)–N(1A)–C(5A)	106.7(6)	N(1B)–C(2B)–C(10B)	123.4(8)
Cu–N(1B)–C(2B)	118.7(6)	N(3B)–C(2B)–C(10B)	125.4(8)
Cu–N(1B)–C(5B)	133.3(6)	N(3B)–C(4B)–C(5B)	105.1(8)
C(2B)–N(1B)–C(5B)	106.0(7)	N(3B)–C(4B)–C(9B)	133.1(9)
C(2A)–N(3A)–C(4A)	108.0(7)	C(5B)–C(4B)–C(9B)	121.8(9)
C(2B)–N(3B)–C(4B)	109.0(7)	N(1B)–C(5B)–C(4B)	108.6(8)
O(1C)–N(C)–O(2C)	117.4(8)	N(1B)–C(5B)–C(6B)	131.0(8)
O(1C)–N(C)–O(3C)	120.3(9)	C(4B)–C(5B)–C(6B)	120.4(8)
O(2C)–N(C)–O(3C)	122.3(9)	C(5B)–C(6B)–C(7B)	117.5(9)
O(1D)–N(D)–O(2D)	119(5)	C(6B)–C(7B)–C(8B)	121.7(9)
O(1D)–N(D)–O(3D)	128(5)	C(7B)–C(8B)–C(9B)	121.5(9)
O(1D)–N(D)–O(2E)	11(1)	C(4B)–C(9B)–C(8B)	117.2(9)
O(1D)–N(D)–O(3E)	122(5)	O(B)–C(10B)–C(2B)	106.8(7)

Each of the Hbim ligands is bidentate, occupying two *cis* octahedral sites, while the co-ordinated $[NO_3]^-$ ligand takes up the remaining *cis* octahedral site. The ligand environment of the copper atom corresponds approximately to a very distorted octahedron. The main components of distortion are a pronounced axial elongation of the type expected from the Jahn–Teller effect, and an angular deviation required by the small bite angle of the bidentate $[NO_3]^-$ ligand. There are four short and two long metal–ligand bonds, with significant angular distortions as well. Because of the asymmetry of the elongated axis, an alternative view of the copper geometry would be as a square pyramid with an off-the-

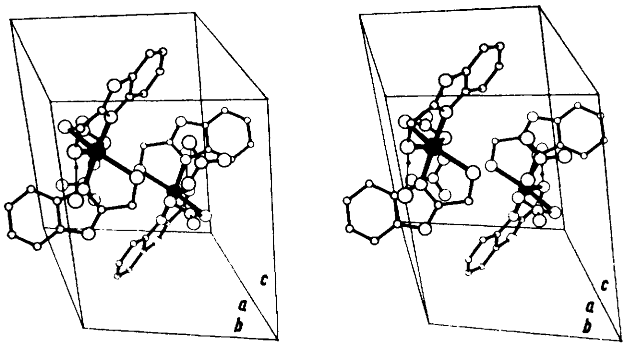

FIGURE 2 Molecular packing in the unit cell of $[Cu(Hbim)_2(NO_3)][NO_3]\cdot H_2O$

z-axis ligand within semi-co-ordination distance.[14] The central ligand plane consists of the four closely bonded ligands, O(A) and N(A) from one of the Hbim ligands, O(1C) from the co-ordinated nitrate, and N(1B) from the other Hbim ligand. It is distorted in the direction of a tetrahedron: the opposite atoms (*trans*) in this plane are either above it (the two oxygens) or below it (the two nitrogens) by *ca.* 0.25 Å in each case. The copper atom is situated 0.14 Å above the centre of the plane. The result of this slight octahedral distortion is to produce O(1C)–Cu–O(A) and N(1A)–Cu–N(1B) angles of 157.6 and 166.0° respectively; true planarity would require 180°. The other two ligand planes [O(B), O(2C), N(1A), N(1B) and O(A), O(B), O(1C), O(2C)] are inclined at 83.1° to one another and at 85.0 and 82.7° respectively to the central ligand plane; regular octahedral or tetragonal geometry would require 90°. The benzimidazole ligand fragments are quite flat: in ligand A the angle between the phenyl and the imidazole rings is 1.0° while in ligand B this angle is 1.6°. The two benzimidazole fragments in ligands A and B are inclined at 66.8° to one another, and at 87.9 and 72.7° respectively to the co-ordinated nitrate group, instead of being orthogonal, which further highlights the distortion from octahedral or tetragonal geometry.

The four short bonds in the principal ligand plane are quite normal for copper(II): mean Cu–O 2.055, mean Cu–N 1.953 Å. The out-of-plane bond to the co-ordinated nitrate is quite weak [Cu–O(2C) 2.498 Å], making the nitrate group bidentate, but only marginally so, a fact of importance in attempts to distinguish between uni- and bidentate nitrate groups attached to Cu^{II}. Such nitrate co-ordination is common for copper(II) [15] as in bis[nitrato-(*N*-ethyl-2-hydroxybenzylideneiminato-μ-*O*)copper(II)] [16] with bond lengths of 1.985 and 2.449 Å to the nitrate group, and contrasts sharply with analogous nitratonickel(II) complexes [17] where both oxygens of the nitrate group tend to be strongly bonded to the metal. The out-of-plane bond to the alcoholic oxygen of ligand B is of intermediate strength [Cu–O(B) 2.284 Å]. The greatest angular distortion is 55.4° for O(1C)–Cu–O(2C) required by the small bite angle of the nitrate group and the elongation of the weakest bond. The Hbim ligand (A) permits an angle of 80.9° at the copper when bonded at the central ligand plane. In the other Hbim ligand, elongation of the metal–oxygen bond reduces this angle to 77.2°.

Table 4 lists the magnetic properties of the complex as a function of temperature. The magnetic susceptibility follows a Curie–Weiss relation in the 4—100 K region (Weiss constant $\theta = -1°$). The polymeric nature of the complex, induced by the hydrogen bonding, must produce finite magnetic interactions. There is a precedent for significant antiferromagnetic interactions, observable at >4 K, in infinite polymeric hydrogen-bonded nickel complexes.[17] However, any interactions in the present complex are so small as to be unobservable even at 4 K; the magnetic moments show no clear trend even at the lowest attainable temperatures. The present results contrast slightly with earlier data [1] obtained *via* the Gouy method in the range 80—350 K. These data show a gradual increase in magnetic moment with increasing temperature ($\mu = 1.78$ B.M.* at 80 K, 1.88 B.M. at 315 K, leading to an antiferromagnetic Weiss constant of $\theta = -14°$). Similar weak antiferromagnetic interactions are implied by data for three analogues of the present complex, although again the trend towards lower moments is small. It seems reasonable to expect that the structures of the four complexes, with closely related ligands, are similar, which would account for the similar magnetic properties. We attribute the difference from the present magnetic data to experimental error, the present Josephson-junction method being the most accurate technique available.

TABLE 4

Magnetic measurements

T/K	4.25	4.63	5.34	6.06	7.08	8.22	9.42	10.8
μ/B.M.	1.83	1.86	1.85	1.86	1.86	1.85	1.87	1.88
T/K	12.2	13.4	14.5	15.9	16.8	17.6	18.4	19.2
μ/B.M.	1.85	1.87	1.84	1.87	1.83	1.83	1.83	1.83
T/K	20.0	20.6	21.3	22.0	23.3	24.1	25.2	26.4
μ/B.M.	1.83	1.83	0.83	1.83	1.83	1.83	1.83	1.83
T/K	29.0	33.0	39.8	48.0	52.0	66.1	71.9	79.4
μ/B.M.	1.84	1.84	1.84	1.83	1.83	1.84	1.81	1.80
T/K	87.0	94.0	101	109				
μ/B.M.	1.80	1.79	1.79	1.79				

Knowledge of the molecular structure aids the assignment of i.r. spectra. Table 5 lists the observed frequencies in the metal–ligand region and their postulated assignments. The assignment of the Cu–N band at 291 cm^{-1} is supported directly, and therefore the other assignments are supported indirectly, by the observation [18] of the Cu–N band in the range 286—292 cm^{-1} for [Cu(imidazole)$_4$]X$_2$ (X = Cl, Br, or NO$_3$) and the observation [19] of the same band at 265—303 cm^{-1} in [LCu(OH)$_2$CuL]$^{2+}$ (L = 2,2′-bipyridine or 1,10-phenanthroline). Likewise the assignment of the band at 242 cm^{-1} to ν_{asym}(Cu–N) is supported by observations of such bands in the same region for a variety of complexes.[20-23]

TABLE 5

Wavenumbers (cm^{-1}) of i.r. bands

	Assignment
329m	Cu–O asym
308m—w	Cu–O sym or ligand
291m—w	Cu–N sym
242w	Cu–N asym

m = Medium, w = weak.

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

REFERENCES

[1] G. J. Hamilton and E. Kokot, *Austral. J. Chem.*, 1973, **26**, 997.

[2] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391.

[3] E. Sinn and W. T. Robinson, *J.C.S. Chem. Comm.*, 1972, 359; R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, 1974, **13**, 2013.

[4] M. A. Phillips, *J. Chem. Soc.*, 1928, 2393; 1929, 2820.

[5] G. K. Hughes and F. Lions, *J. Proc. Roy. Soc. New South Wales*, 1937—1938, **71**, 209.

[6] E. J. Cukauskas, B. S. Deaver, jun., and E. Sinn, *J. Chem. Phys.*, 1977, **67**, 1257.

[7] J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 269.

[8] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[9] D. T. Cromer and J. T. Waber, ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. **4**, section 2.2.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1975, **42**, 3175.

[11] D. T. Cromer and J. A. Ibers, ref. 9, section 2.3.

[12] D. P. Freyberg, G. M. Mockler, and E. Sinn, *J.C.S. Dalton*, 1976, 447.

[13] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[14] B. J. Hathaway, *Structure and Bonding*, 1973, **14**, 49.

[15] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[16] E. Sinn, *Inorg. Chem.*, 1976, **15**, 366.

[17] R. J. Butcher and E. Sinn, *J.C.S. Chem. Comm.*, 1975, 832; R. J. Butcher, J. Jasinski, G. M. Mockler, and E. Sinn, *J.C.S. Dalton*, 1976, 1099.

[18] W. J. Eilbeck, F. Holmes, C. E. Taylor, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1968, 128.

[19] J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, 1965, **4**, 1382.

[20] M. Biddau, M. Massacesi, R. Pinna, and G. Ponticelli, *Transition Metal Chem.*, 1977, **2**, 5.

[21] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, 1965, **21**, 105.

[22] W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2573.

[23] G. Devoto, M. Massacesi, and G. Ponticelli, *J. Inorg. Nuclear Chem.*, 1977, **39**, 271.