Structure of the Imidazolate-Bridged Dicopper(II) Cation Cu₂(bpim)³⁺

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The structure of [Cu₂(bpim)(NO₃)₂(ClO₄)(H₂O)]·H₂O, where bpim is the ligand 4,5-bis[(2-(2-pyridyl)ethylimino)-methyl]imidazolate, has been determined in an X-ray diffraction study. Each copper atom is coordinated to four approximately planar donor atoms. Three of these are contributed by the bpim ligand, with average Cu–N distances of 1.964 (7) Å for the bridging imidazolate ion, 1.999 (11) Å for the imine nitrogen atoms, and 2.002 (13) Å for the pyridine nitrogen atoms. The fourth sites are occupied by oxygen atoms of bidentate nitrate ligands, the average Cu–O bond lengths being 2.012 (6) Å. Weakly coordinated in the axial positions are the other oxygen atoms of the bidentate nitrate ligands, Cu–O = 2.566 (7) and 2.408 (7) Å, and either a water molecule [Cu–O = 2.356 (8) Å] or a perchlorate oxygen atom [Cu–O = 2.610 (12) Å]. An interesting feature of the structure is the geometry of the 4,5-disubstituted imidazolate ring and the two copper centers. Because of the constraints of the five-membered chelate rings, the imidazolate ring is nearly coplanar with the two principal CuN₃O coordination planes. The two N–Cu–N chelate ring angles are both 81.5 (3)°, and the Cu–N(imidazolate) vectors intersect at an angle of 169.6°. The compound crystallizes in the triclinic system, space group *P*1̄, with *a* = 12.673 (2) Å, *b* = 13.919 (2) Å, *c* = 8.086 (2) Å, α = 102.64 (1)°, β = 96.22 (1)°, γ = 94.25 (1)°, and *Z* = 2.

Introduction

Recent studies in this laboratory have led to the synthesis and characterization of several imidazolate-bridged dicopper(II) complexes.[1,2] These compounds have antiferromagnetically coupled binuclear copper centers with coupling constants in the range $-20 > J > -90$ cm^{-1}.[3,4] Since the variability in J most likely reflects the geometric details of the imidazolate-bridged dicopper(II) center, we have structurally characterized key members of this class of compounds. Here we report the geometry of the Cu₂bpim³⁺ cation (**1**) in which the bridging imidazolate ligand is constrained to be nearly coplanar with the two copper coordination planes.

Cu₂bpim³⁺

1
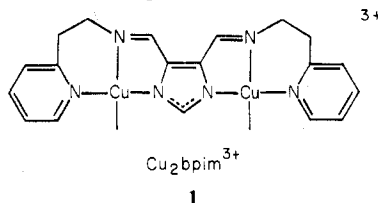
Experimental Section and Results

Collection and Reduction of X-ray Data. Crystals suitable for X-ray study were obtained by dissolving [Cu₂(bpim)(NO₃)₃]·2H₂O⁵[5] in methanol, adding a stoichiometric amount or an excess of NaClO₄·6H₂O, and vapor diffusing in tetrahydrofuran. The dark blue crystal used for the diffraction study was an approximate hexagonal prism bounded by (100) and (1̄00) (0.30 mm apart), (010) and (01̄0) (0.30 mm apart), (001) and (001̄) (0.266 mm apart), and (101) and (1̄01̄) (0.166 mm apart). Preliminary precession and Weissenberg photographs using Cu Kα radiation (λ 1.5418 Å) showed the lattice to have Laue symmetry 1̄, consistent with space group C_i^1-P1 and C_i^1-P1̄.[6] A systematic search using TRACER-II[7] failed to reveal any higher symmetry, and space group *P*1̄ was assumed, a choice that appears to be justified on the basis of the successful refinement of the structure. The quality of the data crystal was found to be acceptable upon taking open-counter ω scans of several strong, low-angle reflections. Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structure. The structure was solved by conventional heavy-atom methods using Patterson and

Fourier maps. Neutral atom scattering factors for the nonhydrogen atoms and corrections for the anomalous dispersion effects for the copper and chlorine atoms were obtained from ref 8. Scattering factors for the hydrogen atoms were those of Stewart et al.[9] All noncarbon and nonhydrogen atoms were refined anisotropically. All nonwater molecule hydrogen atoms were placed in calculated positions (C–H = 0.95 Å). The two hydrogen atoms attached to OW(1) were located in a difference Fourier map; those attached to OW(2) could not be located. All hydrogens were included in the refinement as invariants with isotropic thermal parameters fixed at 5 Å², a value one larger than the average isotropic temperature factor for the carbon atoms.

Elemental analyses performed on several batches of crystals gave varying results, suggesting that different batches of crystals might contain different amounts of solvent of crystallization.[10] Residual tetrahydrofuran and methanol were required to fit the analytical data for some batches, while in others only partial methanol seemed likely. The crystal on which this diffraction study was performed had, from the structure analysis itself, the composition [Cu₂(bpim)(NO₃)₂-(ClO₄)(H₂O)]·H₂O. Evidence for partial methanol or tetrahydrofuran occupancy was not found. The highest peak on a final difference Fourier map was 0.88 e Å^{-3}, located 2.51 Å from OW(2). All remaining peaks on this map were less than 0.67 e Å^{-3} on a scale where a typical carbon atom was 4.21 e Å^{-3}.

In the final cycle of refinement, no parameter shifted by more than 0.004 of its estimated standard deviation except for OW(2) where the largest shift was 0.04σ, for β_{33}. The discrepancy indices R_1 and R_2 converged at 0.060 and 0.063, respectively.[11] The function $\sum w\Delta^2$ for groups of data sectioned according to $|F_o|$ or $(\sin\theta)/\lambda$ showed reasonable consistency, and the weighting scheme was considered to be satisfactory.[12] The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO = 2371 independent observations and NV = 284 variables, was 1.733 at convergence.[12]

The final atomic positional parameters, together with their standard deviations, are reported in Table II. The interatomic distances and angles, with standard deviations, appear in Table III. A listing of the final observed and calculated structure factor amplitudes, thermal parameters, the root-mean-square amplitudes of thermal vibration for anisotropically refined atoms, and the results of least-squares plane calculations are available as Tables S1–S4, respectively.[13] The geometry of the cation and the atom labeling scheme are shown in Figure 1. Figure 2 displays a unit-cell packing diagram.

(1) Lippard, S. J.; Burger, A. R.; Ugurbil, K.; Valentine, J. S.; Pantoliano, M. W. *Adv. Chem. Ser.* **1977**, *No. 162*, 251.
(2) O'Young, C-L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291.
(3) Kolks, G.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5804.
(4) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622.
(5) Kolks, G.; Frihart, C. R.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5720.
(6) "International Tables for X-ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England, 1965; Vol. I, pp 74–5.
(7) Lerner, E. I.; Lippard, S. J. *Inorg. Chem.* **1977**, *16*, 1546 (see Table I, footnote c, for a list of computer programs used in this work).

(8) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 149.
(9) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(10) Kolks, G.; Lippard, S. J., to be submitted for publication.
(11) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. In the least-squares refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized.
(12) Cruickshank, D. W. J. In "Computing Methods of Crystallography"; Rollet, J. S., Ed.; Pergamon Press: Elmsford, N.Y., 1965; pp 112–5.
(13) Supplementary material.

Table I. Experimental Details of the X-ray Diffraction Study of
[Cu$_2$(bpim)(NO$_3$)$_2$(ClO$_4$)(H$_2$O)]·H$_2$O

(A) Crystal Parameters at 23 °C

Cell Used for Data Collection, Reduction, and Structure Solution

$a = 12.648$ (9) Å	$\alpha = 110.25$ (3)°
$b = 8.065$ (6) Å	$\beta = 97.48$ (4)°
$c = 14.454$ (9) Å	$\gamma = 83.89$ (3)°

Reduced Cell^a Used in Final Refinement

$a = 12.673$ (2) Å	$\alpha = 102.64$ (1)°
$b = 13.919$ (2) Å	$\beta = 96.22$ (1)°
$c = 8.086$ (2) Å	$\gamma = 94.25$ (1)°

General Parameters

transformation matrix to reduced   mol wt 718.0
  cell: (100, 0̄11, 01̄0) $V = 1376.5$ Å^3
space group $P\bar{1}$ ρ(calcd) = 1.732 g cm^{-3}
$Z = 2$ ρ(obsd)^b = 1.703 (1) g cm^{-3}

(B) Measurement of Intensity Data

instrument: Picker FACS-I-DOS diffractometer
radiation: Mo Kα (λ_{α_1} 0.7093 Å), graphite monochromatized
takeoff angle: 2.0°
detector aperture: 6.3 × 6.3 mm
cryst–detector distance: 33 cm
scan technique: coupled θ(crystal)–2θ(detector)
scan range: 2.0° (symmetric, plus Kα_1–Kα_2 dispersion)
scan rate: 2°/min in 2θ
max 2θ: 45°, above which there were few observable
  reflections
bgd measurements: stationary crystal, stationary counter;
  20-s counts at each end of the 2θ scan range
stds: three reflections (2̄10), (401), and (1̄10) measured after
  every 97 data reflections showed only random statistical
  fluctuations
no. of reflctns collected: [2θ < 20° (±h, ±k, ±l), 20 < 2θ <
  45° (±h, ±k, +l)]; 3544 reflctns

(C) Treatment of Intensity Data^c

reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for
  background, attenuators, and Lorentz–polarization effect of
  monochromatized X-radiation in the usual manner;^{d}
  $\epsilon = 0.04^e$
absorption correction: $\mu = 17.2$ cm^{-1}; transmission factors
  varied from 0.55 to 0.77
averaging: 456 equivalent pairs in the inner sphere (2θ ≤ 20°);
  agreement factor $R_{av}{}^f = 0.013$
scaling: Wilson's method;^{g} $\bar{B} = 3.24$ Å^2
obsd data: 2371 unique reflctns for which $F_o^2 > 2\sigma(F_o^2)$

^{a} From a least-squares fit to the setting angles of 25 reflections
(2θ > 30°) measured on an Enraf-Nonius CAD-4F κ-geometry
diffractometer. ^{b} By suspension in a mixture of bromoform and
carbon tetrachloride. ^{c} Reference 7. ^{d} Gill, J. T.; Lippard, S. J.
Inorg. Chem. 1975, *14*, 751. ^{e} Corfield, P. W. R.; Doedens, R. J.;
Ibers, J. A. *Ibid.*, 1967, *6*, 197. ^{f} $R_{av} = [(\Sigma_{i=1}{}^N \Sigma_{j=1}{}^n \bar{F}_i{}^2 - F_{ij}{}^2|)/\Sigma_{i=1}{}^N \bar{F}_i{}^2]$, where N is the number of reflections measured
more than once and n is the number of observations of the Nth re-
flection. ^{g} Wilson, A. J. C. *Nature (London)* 1942, *150*, 151.
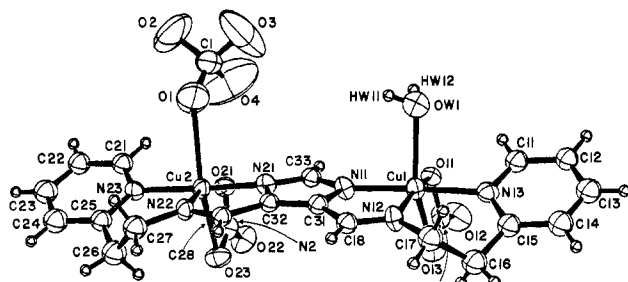
Figure 1. View of [Cu$_2$(bpim)(NO$_3$)$_2$(ClO$_4$)(H$_2$O)] showing the atom
labeling scheme. Thermal ellipsoids are depicted at the 40% probability
level for all atoms except hydrogen which are assigned as arbitrary
spheres having $B = 1.0$ Å^2.

Discussion

The structure consists of discrete [Cu$_2$(bpim)(NO$_3$)$_2$-
(ClO$_4$)(H$_2$O)] units (Figure 1) and water molecules of crys-

Table II. Final Positional Parameters of the Atoms of
[Cu$_2$(bpim)(NO$_3$)$_2$(ClO$_4$)(H$_2$O)]·H$_2$O^a

atom	x	y	z
Cu(1)	0.29311 (9)	−0.27528 (8)	−0.40565 (14)
Cu(2)	0.17163 (9)	0.12982 (8)	−0.04751 (13)
Cl	0.4131 (3)	0.2392 (3)	−0.1598 (5)
O(1)	0.3649 (11)	0.2121 (8)	−0.0365 (15)
O(2)	0.4489 (14)	0.3371 (10)	−0.1160 (17)
O(3)	0.4916 (13)	0.1955 (13)	−0.221 (2)
O(4)	0.3388 (14)	0.2233 (14)	−0.296 (2)
N(1)	0.1517 (8)	−0.2925 (7)	−0.6827 (12)
O(11)	0.2472 (6)	−0.2487 (5)	−0.6362 (8)
O(12)	0.1113 (6)	−0.2965 (7)	−0.8293 (10)
O(13)	0.1075 (6)	−0.3271 (5)	−0.5775 (9)
N(2)	0.0104 (8)	0.1042 (6)	−0.2832 (11)
O(21)	0.1048 (6)	0.1455 (5)	−0.2761 (7)
O(22)	−0.0527 (6)	0.0969 (5)	−0.4120 (9)
O(23)	−0.0113 (5)	0.0711 (5)	−0.1588 (9)
N(11)	0.2607 (6)	−0.1465 (6)	−0.2757 (9)
N(12)	0.3004 (6)	−0.3059 (5)	−0.1733 (9)
N(13)	0.3289 (6)	−0.4117 (6)	−0.5135 (9)
N(21)	0.2250 (6)	0.0035 (5)	−0.1435 (9)
N(22)	0.2026 (6)	0.0845 (5)	0.1678 (8)
N(23)	0.1285 (6)	0.2591 (5)	0.0707 (9)
OW(1)	0.4707 (6)	−0.2131 (6)	−0.4091 (10)
OW(2)	0.5136 (12)	−0.0326 (16)	−0.175 (3)
C(11)	0.3751 (8)	−0.4211 (8)	−0.6557 (12)
C(12)	0.4054 (8)	−0.5098 (8)	−0.7424 (12)
C(13)	0.3857 (8)	−0.5904 (8)	−0.6779 (13)
C(14)	0.3403 (8)	−0.5833 (8)	−0.5342 (13)
C(15)	0.3092 (8)	−0.4941 (8)	−0.4521 (12)
C(16)	0.2570 (8)	−0.4824 (8)	−0.2933 (13)
C(17)	0.3150 (8)	−0.4033 (8)	−0.1450 (13)
C(18)	0.2831 (7)	−0.2349 (7)	−0.0552 (11)
C(21)	0.1416 (8)	0.3359 (7)	−0.0002 (12)
C(22)	0.1108 (8)	0.4280 (8)	0.0676 (13)
C(23)	0.0663 (8)	0.4409 (8)	0.2159 (14)
C(24)	0.0537 (8)	0.3626 (8)	0.2925 (13)
C(25)	0.0847 (7)	0.2703 (7)	0.2184 (12)
C(26)	0.0721 (8)	0.1839 (8)	0.2985 (13)
C(27)	0.1740 (8)	0.1378 (7)	0.3322 (12)
C(28)	0.2272 (7)	−0.0020 (7)	0.1488 (11)
C(31)	0.2650 (7)	−0.1444 (7)	−0.1039 (11)
C(32)	0.2419 (7)	−0.0523 (6)	−0.0241 (11)
C(33)	0.2360 (7)	−0.0573 (7)	−0.2918 (11)
H(11)	0.388	−0.364	−0.700
H(12)	0.439	−0.514	−0.843
H(13)	0.404	−0.653	−0.736
H(14)	0.329	−0.640	−0.488
H(161)	0.254	−0.544	−0.260
H(162)	0.187	−0.465	−0.318
H(171)	0.389	−0.412	−0.134
H(172)	0.287	−0.410	−0.043
H(18)	0.282	−0.242	0.059
H(21)	0.174	0.327	−0.103
H(22)	0.120	0.481	0.012
H(23)	0.044	0.503	0.266
H(24)	0.024	0.371	0.397
H(261)	0.045	0.205	0.404
H(262)	0.022	0.135	0.224
H(271)	0.229	0.188	0.387
H(272)	0.164	0.093	0.403
H(28)	0.236	−0.033	0.242
H(33)	0.227	−0.039	−0.398
HW(11)	0.488	−0.165	−0.331
HW(12)	0.470	−0.177	−0.487

^{a} Atoms are labeled as indicated in Figure 1. Estimated stand-
ard deviations, in parentheses, occur in the last significant figure
for each parameter. Hydrogens are labeled such that H(ij) is the
jth H on C(i). HW(11) and HW(12) are attached to OW(1).

tallization in a 1:1 ratio (Figure 2). In the equatorial plane,
each copper atom is bound by three nitrogen atoms of the
bridging bpim ligand [Cu–N(imidazolate) = 1.966 (7) and
1.961 (7) Å; Cu–N(imine) = 2.010 (7) and 1.988 (7) Å;
Cu–N(pyridine) = 2.015 (7) and 1.989 (7) Å]. The remaining
equatorial site and one axial site of each copper are occupied

Table III. Interatomic Distances (Å) and Angles (Deg) for [Cu₂(bpim)(NO₃)₂(ClO₄)(H₂O)]·H₂O[a]

Distances

Coordination Geometry

Cu(1)-N(11)	1.966 (7)	Cu(2)-N(21)	1.961 (7)	Cu(1)-O(11)	2.012 (6)	Cu(2)-O(21)	2.011 (6)
Cu(1)-N(12)	2.010 (7)	Cu(2)-N(22)	1.988 (7)	Cu(1)-O(13)	2.566 (7)	Cu(2)-O(23)	2.408 (7)
Cu(1)-N(13)	2.015 (7)	Cu(2)-N(23)	1.989 (7)	Cu(1)-OW(1)	2.356 (8)	Cu(2)-O(1)	2.610 (12)

Ligand Geometry

N(13)-C(11)	1.33 (1)	N(23)-C(21)	1.33 (1)	C(16)-C(17)	1.52 (1)	C(26)-C(27)	1.51 (1)
C(11)-C(12)	1.38 (1)	C(21)-C(22)	1.38 (1)	C(17)-N(12)	1.44 (1)	C(27)-N(22)	1.47 (1)
C(12)-C(13)	1.35 (1)	C(22)-C(23)	1.36 (1)	N(12)-C(18)	1.26 (1)	N(22)-C(28)	1.25 (1)
C(13)-C(14)	1.34 (1)	C(23)-C(24)	1.37 (1)	C(18)-C(31)	1.43 (1)	C(28)-C(32)	1.46 (1)
C(14)-C(15)	1.38 (1)	C(24)-C(25)	1.40 (1)	C(31)-N(11)	1.38 (1)	C(32)-N(21)	1.37 (1)
C(15)-N(13)	1.36 (1)	C(25)-N(23)	1.35 (1)	N(11)-C(33)	1.33 (1)	N(21)-C(33)	1.34 (1)
C(15)-C(16)	1.49 (1)	C(25)-C(26)	1.49 (1)			C(31)-C(32)	1.37 (1)
N(1)-O(11)	1.29 (1)	N(2)-O(21)	1.28 (1)	Cl-O(1)	1.33 (1)	Cl-O(3)	1.29 (1)
N(1)-O(12)	1.23 (1)	N(2)-O(22)	1.224 (9)	Cl-O(2)	1.36 (1)	Cl-O(4)	1.34 (1)
N(1)-O(13)	1.23 (1)	N(2)-O(23)	1.243 (9)				

Hydrogen-Bonded and Nonbonded Contacts

OW(1)-HW(11)	0.814 (8)	OW(2)···HW(11)	1.97 (2)	OW(1)···OW(2)	2.77 (2)	OW(2)···OW(2)[b]	2.85 (4)
OW(1)-HW(12)	0.889 (8)	OW(2)···HW(12)	2.83 (2)	Cu(1)···Cu(2)	6.137 (2)	Cu(2)···Cu(2)[c]	5.673 (3)

Angles

Coordination Geometry

N(11)-Cu(1)-N(12)	81.5 (3)	N(21)-Cu(2)-N(22)	81.5 (3)	N(12)-Cu(1)-OW(1)	101.7 (3)	N(22)-Cu(2)-O(1)	94.6 (4)
N(11)-Cu(1)-N(13)	173.6 (3)	N(21)-Cu(2)-N(23)	174.1 (3)	N(13)-Cu(1)-O(11)	91.5 (3)	N(23)-Cu(2)-O(21)	91.8 (3)
N(11)-Cu(1)-O(11)	94.9 (3)	N(21)-Cu(2)-O(21)	93.7 (3)	N(13)-Cu(1)-O(13)	86.3 (3)	N(23)-Cu(2)-O(23)	90.9 (3)
N(11)-Cu(1)-O(13)	96.6 (3)	N(21)-Cu(2)-O(23)	93.7 (3)	N(13)-Cu(1)-OW(1)	89.3 (3)	N(23)-Cu(2)-O(1)	90.0 (3)
N(11)-Cu(1)-OW(1)	91.5 (3)	N(21)-Cu(2)-O(1)	87.0 (3)	O(11)-Cu(1)-O(13)	54.7 (3)	O(21)-Cu(2)-O(23)	57.5 (3)
N(12)-Cu(1)-N(13)	92.0 (3)	N(22)-Cu(2)-N(23)	93.7 (3)	O(11)-Cu(1)-OW(1)	91.9 (3)	O(21)-Cu(2)-O(1)	101.0 (4)
N(12)-Cu(1)-O(11)	166.0 (3)	N(22)-Cu(2)-O(21)	163.5 (3)	O(13)-Cu(1)-OW(1)	146.1 (3)	O(23)-Cu(2)-O(1)	158.5 (3)
N(12)-Cu(1)-O(13)	112.0 (3)	N(22)-Cu(2)-O(23)	106.8 (3)				

Ligand Geometry

Cu(1)-N(13)-C(11)	116.9 (7)	Cu(2)-N(23)-C(21)	118.4 (6)	C(17)-N(12)-C(18)	122.3 (8)	C(27)-N(22)-C(28)	120.6 (8)
Cu(1)-N(13)-C(15)	125.0 (6)	Cu(2)-N(23)-C(25)	122.1 (6)	C(17)-N(12)-Cu(1)	122.9 (6)	C(27)-N(22)-Cu(2)	122.7 (6)
C(15)-N(13)-C(11)	118.1 (8)	C(25)-N(23)-C(21)	119.4 (8)	Cu(1)-N(12)-C(18)	114.6 (6)	Cu(2)-N(22)-C(28)	115.0 (6)
N(13)-C(11)-C(12)	123.3 (9)	N(23)-C(21)-C(22)	123.2 (9)	N(12)-C(18)-C(31)	116.0 (8)	N(22)-C(28)-C(32)	116.3 (9)
C(11)-C(12)-C(13)	117.4 (9)	C(21)-C(22)-C(23)	118.3 (10)	C(18)-C(31)-N(11)	116.3 (8)	C(28)-C(32)-N(21)	114.2 (8)
C(12)-C(13)-C(14)	120.8 (10)	C(22)-C(23)-C(24)	119.2 (10)	C(18)-C(31)-C(32)	136.3 (8)	C(28)-C(32)-C(31)	136.6 (9)
C(13)-C(14)-C(15)	120.4 (10)	C(23)-C(24)-C(25)	120.6 (9)	N(11)-C(31)-C(32)	107.2 (7)	N(21)-C(32)-C(31)	109.2 (7)
C(14)-C(15)-C(16)	122.7 (10)	C(24)-C(25)-C(26)	121.9 (9)	C(31)-N(11)-Cu(1)	111.3 (6)	C(32)-N(21)-Cu(2)	112.1 (5)
C(14)-C(15)-N(13)	119.9 (9)	C(24)-C(25)-N(23)	119.2 (9)	C(31)-N(11)-C(33)	105.6 (7)	C(32)-N(21)-C(33)	104.6 (7)
C(16)-C(15)-N(13)	117.4 (8)	C(26)-C(25)-N(23)	119.0 (8)	Cu(1)-N(11)-C(33)	143.0 (6)	Cu(2)-N(21)-C(33)	142.2 (7)
C(15)-C(16)-C(17)	113.7 (9)	C(25)-C(26)-C(27)	114.3 (9)			N(11)-C(33)-N(21)	113.4 (8)
C(16)-C(17)-N(12)	110.4 (8)	C(26)-C(27)-N(22)	108.4 (8)				
Cu(1)-O(11)-N(1)	105.7 (6)	Cu(2)-O(21)-N(2)	101.3 (6)	Cu(1)-OW(1)-HW(12)	107.7 (6)	O(1)-Cl-O(2)	111.2 (8)
Cu(1)-O(13)-N(1)	81.1 (6)	Cu(2)-O(23)-N(2)	83.7 (6)	HW(11)-OW(1)-HW(12)	91.8 (7)	O(1)-Cl-O(3)	122.4 (10)
O(11)-N(1)-O(12)	117.5 (9)	O(21)-N(2)-O(22)	119.1 (9)	O(1)-Cl-O(4)	106.0 (10)	O(2)-Cl-O(4)	108.6 (11)
O(11)-N(1)-O(13)	118.0 (9)	O(21)-N(2)-O(23)	117.5 (8)	O(2)-Cl-O(3)	104.9 (11)	O(3)-Cl-O(4)	102.7 (12)
O(12)-N(1)-O(13)	124.5 (10)	O(22)-N(2)-O(23)	123.4 (10)			OW(1)-HW(11)-OW(2)	168 (1)
Cu(1)-OW(1)-HW(11)	110.1 (6)	Cu(2)-O(1)-Cl	129.7 (9)				

[a] Atoms are labeled as indicated in Figure 1. Estimated standard deviations, in parentheses, occur in the last significant figure for each parameter. Values reported have not been corrected for thermal motion. [b] Atom is at (1 − x, −y, −z). [c] Atom is at (−x, −y, −z).
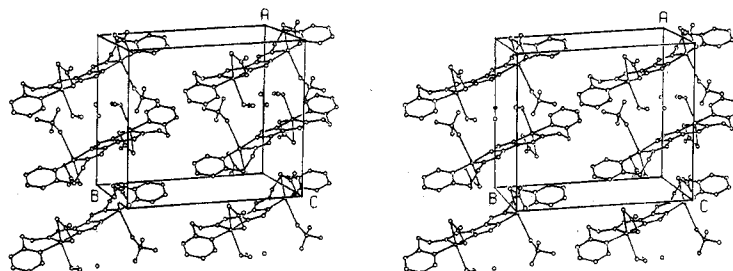

Figure 2. Unit-cell packing diagram for [Cu₂(bpim)(NO₃)₂(ClO₄)(H₂O)]·H₂O. The two molecules in the upper right of the cell may be linked by a weak hydrogen-bonding network across a center of symmetry. The same situation holds for the pair of molecules in the upper left of the cell.

by oxygen atoms of bidentate nitrate ligands, with both nitrate anions lying on the same side of the bpim ligand plane [Cu–O(equatorial) = 2.012 (6) and 2.011 (6) Å; Cu–O(axial) = 2.566 (7) and 2.408 (7) Å]. The oxygen atom of a water molecule is bound in the sixth site of Cu(1) [Cu–OW(1) = 2.356 (8) Å] and an oxygen atom of the perchlorate anion

occupies the sixth site of Cu(2) [Cu–O(1) = 2.610 (12) Å].

The imidazolate ring of the bpim ligand is constrained to lie almost parallel with the equatorial coordination planes of the two copper atoms. The dihedral angles between the imidazolate ring plane and the copper coordination planes are 4.69° for Cu(1) and 13.37° for Cu(2). The angle between

the coordination planes themselves is 8.84°. By comparison, the angle between the copper coordination planes in $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$, where TMDT is 1,1,7,7-tetramethyldiethylenetriamine and im is the imidazolate ion, is 148.7°.[2] In this latter complex the two copper coordination planes are not constrained to be coplanar with the imidazolate ring, the dihedral angles between this ring plane and the coordination planes being 91.8 and 90.0°. Another consequence of the constraints imposed by the bpim ligand can be seen in the larger angle between the Cu–N(imidazolate) vectors which is 169.6° in the present compound and 143.2° in $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$.

At present we cannot be absolutely certain about which of the above two structural differences between Cu_2bpim^{3+} ($J = -81.3$ cm^{-1})[3] and $[(TMDT)_2Cu_2(im)(ClO_4)_2]^+$ ($J = -25.8$ cm^{-1})[2] is responsible for their different magnetic exchange coupling constants. Magnetic and structural work on a series of dicopper(II) complexes having substituted imidazolate bridges of differing σ-donor ability has established a correlation between the pK_a of the bridging ligand and J.[10] It is therefore likely that the difference in the angle between the Cu–N(imidazolate) vectors, and not the dihedral angle differences, is the more important factor in determining J. The former would involve a σ-exchange mechanism whereas the latter would effect a π-exchange pathway.[3]

The five atoms comprising the imidazolate ring lie within 0.007 Å of the best plane through them. Cu(1) is 0.023 Å out of this plane while Cu(2) is 0.261 Å away and on the opposite side. Similar deviations occur in the structure of $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$, where the two copper atoms are 0.02 and 0.35 Å out of the plane of the bridging imidazolate anion. The atoms in the pyridine rings of the bpim ligand deviate less than 0.01 Å, in either case, from the best plane through their respective pyridine ring atoms. C(16) and C(26) lie close to these planes [0.01 (1) Å] but, as is evident in Figure 1, the puckering of the bpim ligand in the vicinity of C(17) and C(27) causes these atoms to be 1.13 and 1.14 Å out of their respective pyridine ring planes. The resulting chelate rings have the asymmetric boat conformation.[14] The nitrate anions are planar with no atom deviating more than 0.008 Å from either best plane.

The Cu–N(imidazolate) distances are comparable with those observed in other structures, the values being 1.944 (12) and 1.966 (14) Å in $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$,[2] 1.984 (10) Å in $[Cu_2(bpim)(im)]_2^{4+}$,[5] 1.976 (7) Å in $Cu_3(imH)_8$-$(im)_2(ClO_4)_4$,[15] and 1.975 (11) Å in $Cu(imH)_2(im)Cl$.[16] The

Cu···Cu intramolecular distance of 6.137 (2) Å is longer than the comparable 5.935 (4) Å distance in $[(TMDT)_2Cu_2$-$(im)(ClO_4)_2](ClO_4)$ as a consequence of the larger angle between the Cu–N(imidazolate) vectors in the present complex. The closest intermolecular Cu···Cu distance is 5.673 (3) Å. Distances within the bpim ligand are normal, and there is good agreement between equivalent bond distances in each half of the ligand. The closest intermolecular contact of the structure is 2.85 (1) Å and is between O(23) of nitrate(2) and C(28) of a bpim ligand located at $(-x, -y, -z)$. All other nonbonded contacts are >3.0 Å.

Distances between the water molecules of the structure suggest that pairs of $[Cu_2(bpim)(NO_3)_2(ClO_4)(H_2O)]$ units are linked across a center of symmetry, by a hydrogen bonding network involving the coordinated water molecule, OW(1), and the water molecule of crystallization, OW(2) (Figure 2). The OW(1)···OW(2) distance is 2.77 (2) Å and HW(11), which is attached to OW(1), is 1.97 (2) Å from OW(2). The distance between OW(2) and OW(2′), which are related by a center of symmetry, is 2.85 (4) Å. These distances indicate weak O–H···O hydrogen bonds.[17]

The variability of elemental analyses of different batches of crystals (vide supra) suggests that their solvent content is variable. The present structure analysis showed only a single water of crystallization in the lattice, whereas analytical data for various batches of crystals could only be fit by invoking partial methanol and/or partial tetrahydrofuran in the lattice.[10] This result suggests that the bulk analyses may not be representative of the composition of individual crystals within a batch, and we also note that the observed and calculated densities for the present compound are not in good agreement (Table I). The occurrence of variable solvent content in crystal lattices is not uncommon.[18]

Supplementary Material Available: Tables S1–S4 reporting respectively the observed and calculated structure factor amplitudes, refined thermal parameters, root-mean-square thermal amplitudes, and dihedral angles and mean plane calculations (20 pages). Ordering information is given on any current masthead page.

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