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Stereochemistry of Imidazolate-Bridged Copper(II) Complexes: $[Cu_2bpim(im)]_2(NO_3)_4.3H_2O$, $C_{44}H_{50}Cu_4N_{20}O_{15}$, $[Cu(pip)]_2(im)(NO_3)_3.2{\cdot}5H_2O$, $C_{29}H_{34}Cu_2N_{11}O_{11{\cdot}5}$, $[Cu(pmdt)]_2(2\text{-}Meim)(ClO_4)_3$, $C_{22}H_{51}Cl_3Cu_2N_8O_{12}$, and $[Cu(pmdt)]_2(Bzim)(ClO_4)_3.H_2O$, $C_{25}H_{53}Cl_3Cu_2N_8O_{13}$*

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Abstract. $[Cu_2bpim(im)]_2(NO_3)_4.3H_2O$ (2), $M_r = 1353{\cdot}2$, tetragonal, $I4_1/a$, $a = b = 27{\cdot}204\,(10)$, $c = 14{\cdot}704\,(6)$ Å, $U = 10.882$ Å^3, $Z = 8$, $D_m = 1{\cdot}650\,(2)$, $D_x = 1{\cdot}652$ Mg m^{-3}, $\mu = 1{\cdot}63$ mm^{-1}, $F(000) = 5520$, final $R = 0{\cdot}059$ for 2816 observed reflections. The tetranuclear cation consists of two Cu_2bpim^{3+} units joined by two bridging im groups and has a crystallographically required twofold axis. Three N atoms of the bpim ligand (Cu—N distances 1·99–2·09 Å) and one N of the im ion [Cu—N 1·967 (5) Å] form the principal copper coordination plane. Two geometrically distinct bridging im groups, one parallel (bpim ligand) and one perpendicular (im ligand) to the copper coordination plane, occur in the complex. Axial sites are occupied by water and nitrate O atoms. $[Cu(pip)]_2(im)(NO_3)_3.2{\cdot}5H_2O$ (3), $M_r = 847{\cdot}8$, monoclinic, $P2_1/c$, $a = 17{\cdot}475\,(5)$, $b = 17{\cdot}809\,(4)$, $c = 23{\cdot}565\,(5)$ Å, $\beta = 105{\cdot}85\,(2)°$, $U = 7054{\cdot}9$ Å^3, $Z = 8$, $D_m = 1{\cdot}581\,(1)$, $D_x = 1{\cdot}596$ Mg m^{-3}, $\mu = 1{\cdot}29$ mm^{-1}, $F(000) = 3629$, final $R = 0{\cdot}105$ for 3181 observed reflections. Each Cu atom is bonded to three N atoms of the pip ligand (Cu—N distances 2·02–2·09 Å) and to one N atom of the bridging, perpendicular-type im ring [av. Cu—N 1·978 (12) Å], all in an approximate plane. Water and nitrate-group O atoms are coordinated at the axial sites. $[Cu(pmdt)]_2(2\text{-}Meim)(ClO_4)_3$ (5), $M_r = 853{\cdot}1$, orthorhombic, $Imm2$, $a = 14{\cdot}226\,(2)$, $b = 16{\cdot}214\,(3)$, $c = 7{\cdot}970\,(2)$ Å, $U = 1838{\cdot}3$ Å^3, $Z = 2$, $D_m = 1{\cdot}544\,(2)$, $D_x = 1{\cdot}541$ Mg m^{-3}, $\mu = 1{\cdot}49$ mm^{-1}, $F(000) = 888$, final $R = 0{\cdot}048$ for 900 observed reflections. $[Cu(pmdt)]_2(Bzim)(ClO_4)_3.H_2O$ (6), $M_r = 907{\cdot}2$, orthorhombic, $Iba2$, $a = 17{\cdot}443\,(5)$, $b = 37{\cdot}510\,(17)$, $c = 12{\cdot}468\,(5)$ Å, $U = 8157{\cdot}7$ Å^3, $Z = 8$, $D_m = 1{\cdot}48\,(1)$, $D_x = 1{\cdot}477$ Mg m^{-3}, $\mu = 1{\cdot}37$ mm^{-1}, $F(000) = 3776$, final $R = 0{\cdot}091$ for 2048 observed reflections. The latter two compounds have bridged binuclear structures with features similar to those of the $[Cu(pip)]_2(im)^{3+}$ cation. The geometric parameters of these four compounds are summarized and compared with related results in the literature.

Introduction. Imidazolate(im)-bridged bimetallic centers are known (Richardson, Thomas, Rubin & Richardson, 1975) or postulated (Palmer, Babcock & Vickery, 1976) to occur in metalloproteins. We have therefore conducted an extensive investigation (Strothkamp & Lippard, 1982) of *M*—im—*M*′ complexes, especially where *M* = *M*′ = Cu, examples of which are depicted in Fig. 1. This paper is the third of a series of three (Kolks, Frihart, Coughlin & Lippard, 1981; Kolks, Lippard, Waszczak & Lilienthal, 1982) and presents the results of structural studies on the complexes shown in Fig. 1. Structural information was desired, not only to verify the existence of the im-bridged dicopper(II) units, but also to examine the relationship between the geometry of the Cu—im—Cu fragments and the magnetic superexchange interactions observed for these compounds. One such relationship had been suggested (Haddad & Hendrickson, 1978) for a related series of Cu_2im^{3+} complexes without the benefit of crystal-structure determinations. Structural investigations of (1) (Dewan & Lippard, 1980) and the *N,N,N″,N″*-tetramethyldiethylenetriamine analogue of (4) (O'Young, Dewan, Lilienthal & Lippard, 1978) were described previously. Here we report the structures of (2), (3), (5) and (6).

Experimental. The crystals used for these studies were obtained as described elsewhere (Kolks *et al.*, 1981). They were mounted on the ends of glass fibers using nail polish or Eastman 910 adhesive. The quality of the data crystals was examined by taking ω scans of several strong, low-angle reflections ($\Delta\omega_{1/2} \sim 0{\cdot}15$–$0{\cdot}21°$). Crystal size and information relevant to data collection and processing are summarized in Table 1. Data collection and computational methods were as

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* Abbreviations used: bpim = 4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazolate, im = imidazolate, pip = 2-[2-(2-pyridyl)-ethyliminomethyl]pyridine, pmdt = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, 2-Meim = 2-methylimidazolate, and Bzim = benzimidazolate.

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described in previous papers from this laboratory (Gill & Lippard, 1975; Silverman, Dewan, Giandomenico & Lippard, 1980).

Crystals of (2) grow as deep-blue tetragonal bipyramids, or fragments of bipyramids, compressed along **c** with the form {101} developed. Oscillation, precession and Weissenberg photographs displayed $4/m$ Laue symmetry. The systematic absences hkl, $h+k+l \neq 2n$; $hk0$, $h(k) \neq 2n$; and $00l$, $l \neq 4n$ are consistent only with space group $I4_1/a$ (C_{4h}^6, No. 88, *International Tables for X-ray Crystallography,* 1965).

Compound (3) crystallized as clusters of greenish-blue monoclinic prisms with the form {012} developed and capped by {100}. The Laue symmetry was determined by film methods to be $2/m$ and the extinction condition, $0k0$, $k \neq 2n$, suggested the space group to be either $P2_1$ or $P2_1/m$. The reflections $h0l$, $l \neq 2n$, were systematically very weak, however, and long (>48 h) exposures were required to observe them on the photographs. The structure was therefore solved and refined in space group $P2_1/c$ (C_{2h}^5, No. 14, *International Tables for X-ray Crystallography,* 1965). Six crystals examined all showed the same violations of the *c*-glide-plane extinction condition, the weak spots being normal Bragg-type (sharp) reflections.

Brown orthorhombic prisms of (5) with the {011} and {110} forms developed and elongated along **c** were studied on the precession and Weissenberg cameras. The *mmm* Laue symmetry and systematic absences hkl, $h+k+l \neq 2n$ were consistent with space groups $I222$ (D_2^8, No. 23), $I2_12_12_1$ (D_2^9, No. 24), $Imm2$ (C_{2v}^{20}, No. 44) and $Immm$ (D_{2h}^{25}, No. 71, *International Tables for X-ray Crystallography,* 1965). Since $Z = 2$, $Imm2$ was recognized to be the correct space group because the site symmetry of the $[Cu(pmdt)]_2(2\text{-Meim})^{3+}$ cation is incompatible, barring disorder, with the symmetry of the twofold special positions in $I222$ or $Immm$. There is no such position in $I2_12_12_1$. Long-exposure (48 h) photographs revealed violations of the body-centering condition that were also present in the data collected by diffractometer. These reflections were weak, and their shape varied from zone to zone. On the $0kl$ zone, they appeared as diffuse streaks extending along [010] whereas on the $h0l$ zone, they appared as a compact 'X' formed by two intersecting streaks. Many of the stronger sharp reflections were surrounded by halos. These results suggest a partially ordered structure in which the disorder involves planes approximately perpendicular to the b axis and the correct space group is not body-centered. In the solution and refinement of the structure the diffuse reflections were disregarded and hence the results presented are the average image of the partially ordered structure.

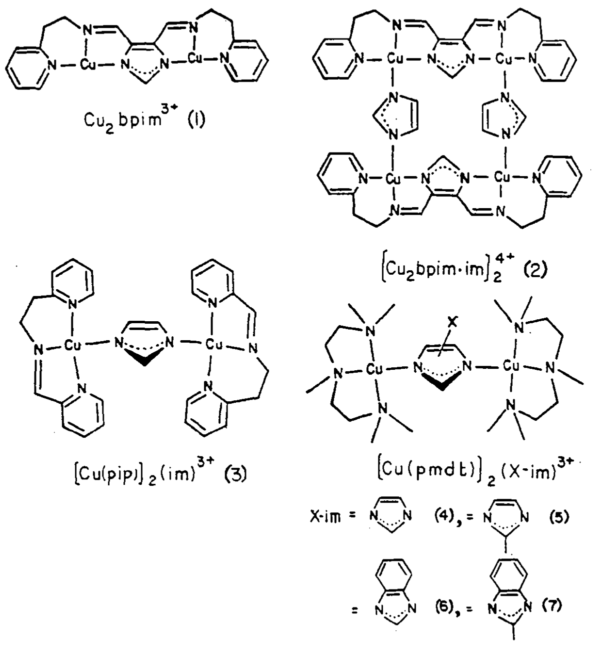

Fig. 1. The im bridged polynuclear copper(II) complexes discussed in this paper.

Compound (6) crystallized as clusters of brown orthorhombic tabular prisms with the forms {010}, {110}, and {121} developed. Examination of six crystals on the Weissenberg camera and of a particularly well developed crystal on the optical goniometer revealed some splitting of reflections on the films and at least two re-entrant (~1° angle) faces (Kolks, 1980). However, ω scans on the diffractometer did not show any structure. The *mmm* Laue symmetry and the extinctions hkl, $h+k+l \neq 2n$; $0kl$, $k(l) \neq 2n$; $h0l$, $h(l) \neq 2n$ are consistent with space groups $Iba2$ (C_{2v}^{21}, No. 45) and $Ibam$ (D_{2h}^{26}, No. 72, *International Tables for X-ray Crystallography,* 1965). The former was chosen based on packing considerations and subsequently confirmed by the successful solution and refinement of the structure.

Determination and refinement of the structures. (2). Structure solved by conventional heavy-atom methods using Patterson and Fourier maps. Refinement proceeded uneventfully to the point described in a preliminary communication (Kolks, Frihart, Rabinowitz & Lippard, 1976). In this and all other structure determinations reported here, neutral-atom scattering factors and anomalous-dispersion corrections were employed (*International Tables for X-ray Crystallography,* 1974). Atoms N(1) to C(6) of the pyridine ring and the exocyclic atom C(7) are disordered over two sites corresponding to rotation about the N(1)–C(4) axis. Atoms C(2), C(3), C(5), C(6) and C(7) were refined isotropically in two positions (*A* and *B*) while all other atoms were refined anisotropically. Although chemical analyses of several subsequent batches of crystals consistently indicated that compound (2) is a tetrahydrate (Kolks, Frihart, Coughlin &

Lippard, 1981), only three water molecules were located crystallographically. Two of these, O(*W*1) and O(*W*1*), are coordinated to the Cu while the third, O(*W*2), is lattice water. The last occupies a 16-fold general position but was given half-occupancy for two reasons: its electron density on difference maps was half that of the coordinated water molecule and full occupancy would have produced an unacceptably short O(*W*2)···O(*W*2*) contact of 2·00 Å. All H atoms attached to ordered atoms were located on difference maps and were included *via* a riding model with C—H fixed at 0·95 Å; the positions of H atoms associated with disordered atoms were fixed with C—H = 0·95 Å; an overall isotropic temperature factor for the H atoms refined to 0·074 (5) Å^2. Inspection of the weighting scheme revealed the r.m.s. deviation of a reflection of unit weight to be three times greater for reflections with $k = 2$ than for any other class. The strong reflection 220 calculated much higher than observed, while the medium-intensity reflections $\bar{1}21$, 121 and $\bar{1}23$ also showed poor agreement between $|F_o|$ and $|F_c|$. These reflections were removed in the final cycles of least-squares refinement with no effect on the geometry. The source of these discrepancies is not known. In the last cycle of full-matrix least-squares refinement none of the 376 parameters varied by more than $0\cdot005\sigma$ with the exception of the parameters associated with nitrate group two, where no parameter shifted by more than $0\cdot05\sigma$. The relative occupancy factor of the two orientations of the disordered methyl pyridine group refined to 0·583 (13) and 0·417 (13) for the atoms labeled *A* and *B* respectively. Largest peak on a final difference Fourier map had a value of 0·86 e Å^{-3} and was located ~1·5 Å from nitrate group two. Discrepancy factors are given in Table 1.

(3) Structure solved by direct methods using *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). There are two formula units per asymmetric unit and two of the nitrate groups are disordered. Consequently 113 non-H atoms form the asymmetric unit. Except for the disorder, there was no apparent reason for the observed violations of the

Table 1. *Experimental details of the X-ray diffraction studies*

Compound	(2)	(5)	(3)	(6)
Temperature (K)	296–299			
Method of measuring D_m	Neutral buoyancy in $CHCl_3/CHBr_3$			
No. of reflections[a]	12	25	25	25
Crystal size[b] (mm)	0·3 × 0·63 × 0·33	0·20 × 0·23 × 0·26	0·13 × 0·19 × 0·22	0·15 × 0·25 × 0·40
Measurement of intensity data				
Instrument	Picker FACS-I-DOS diffractometer		Enraf–Nonius CAD-4F kappa geometry diffractometer	
Radiation	Mo *K*α ($\lambda\alpha$, = 0·70930, $\lambda\bar{\alpha}$ = 0·71073 Å), graphite-monochromatized			
Take-off angle (°)	1·75	1·0	1·50	1·50
Crystal–detector distance (mm)	330	330	173	173
Detector aperture (mm)	6 × 6	4 × 4	Vertical, 4·0; horizontal, variable = 3 + tanθ	
Scan technique	Coupled θ(crystal)–2θ(detector)			
Scan width (°)	1·5 in 2θ plus $K\alpha_1$-$K\alpha_2$ dispersion	2·5 in 2θ plus $K\alpha_1$-$K\alpha_2$ dispersion	0·8 + 0·35 tanθ in ω	
Scan rate (° min^{-1})	1 in 2θ		Variable, 1·4–20·2 in ω	
$2\theta_{\max}$ (°)	50	55	50	55
Background measurements	Stationary crystal/stationary counter; 20 s counts at each end of 2θ range		Moving crystal/moving detector, 25% added to scan width at both ends of scan	
Standards	Three strong, low-angle reflections, well separated from each other in reciprocal space checked every 97 reflections		200, 020, 002; 200, 040, 002 checked after every 3600 s of X-ray exposure	
No. of reflections collected	7043	13280	2457	6348 ($h + k + l = 2n$)
Details of data processing and structure refinement				
	Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators and Lorentz–polarization in the usual manner[c]			
Ignorance factor (ε)[d]	0·05	0·04	0·04	0·0[e]
Absorption correction	Yes	None	None	Yes
Transmission factors	Max. = 0·72; min. = 0·37	Max. = 0·82; min. = 0·79		Max. = 0·82; min. = 0·75
No. of unique data[f]	4056	1133	9050	3923
Data with $F_o \geq n\sigma(F_o)$	2816, $n = 4$	900, $n = 4$	3181, $n = 5$	2048, $n = 4$
No. of variable parameters	376	136	477 in two blocks	295
R_1	0·059	0·048	0·105	0·091
R_2[g]	0·062	0·048	0·090	0·081
κ[g]	1·86	1·17	4·39	2·76

Notes: (*a*) Number of reflections used in the least-squares refinement of the crystal parameters. (*b*) The crystals were mounted approximately along the third dimension reported (*c*). Using *PROCESS* written by P. W. R. Corfield. (*d*) Corfield, Doedens & Ibers (1967). (*e*) See (*g*) below. (*f*) Number of unique, non-space-group-extinguished reflections having $F_o > 0$. (*g*) The function minimized during the least-squares refinement of the structure was $\sum w(|F_o| - |F_c|)^2$ where $w = \kappa[\sigma^{-2}(F_o) + g|F_o|^2]^{-1}$, where κ was refined and g was set equal to zero for (2), (3) and (5) (since $g = \varepsilon^2/4$) and refined to a value of 0·00061 for (6). The analysis of variance as a function of θ, $|F_o|$, $|h|$, $|k|$ and $|l|$ showed good consistency in all four structures indicating that satisfactory weighting schemes had been employed.

glide-plane extinctions (see above). No unusually close intermolecular contacts were noted. Because of the large number of atoms and computer-space limitations, refinement was carried out in $P2_1/c$. The Cu atoms were assigned anisotropic temperature factors and all other atoms were refined isotropically. No H atoms were included. Blocked least-squares refinement was employed. Two blocks were assigned, each consisting of a $[Cu(pip)]_2(im)^{3+}$ group, the nitrate ions, and two or three water O atoms. In the last cycle of refinement for each block no parameter moved by more than $0{\cdot}018\sigma$, except for those of nitrate group three. No parameter of this group moved more than $0{\cdot}08\sigma$, with the average shift being $0{\cdot}036\sigma$. The relative occupancy factors for the disordered nitrate groups refined to 0·56 (6) and 0·44 (6) for the two orientations of nitrate group three and 0·64 (4) and 0·36 (4) for the two orientations of nitrate group five. A final difference map showed no features outside the range $\pm 0{\cdot}76$ e Å^{-3}. The final refinement conditions and residuals are given in Table 1.

(5). In space group *Imm*2 with $Z = 2$ the Cu atom in the asymmetric unit must lie on one of the mirror planes at *x*0*z* or 0*yz*. From packing considerations based upon the unit-cell parameters and the estimated size of the $[Cu(pmdt)]_2(2\text{-}Meim)^{3+}$ cation, the Cu atom was initially placed at (0·209, 0, 0·25). The *z* coordinate of the origin is arbitrary in this space group. The Fourier map phased with this copper position had the expected *Immm* symmetry, but it was possible to identify the two images of the imidazolate ring and pmdt ligand. The remaining atoms were readily found on a difference map phased with these atoms. Perchlorate group two [Cl(2), O(21), O(22), O(23)] is disordered across the mirror planes perpendicular to [010] with the distance between the two images of Cl(2) being 0·49 (13) Å. The images of Cl(2) were not resolved on the difference Fourier maps but were suggested by, and preliminary Cl(2) coordinates were obtained from, the locations of the attached O atoms. All H atoms were located on a difference Fourier map and were constrained to ideal geometric positions in the least-squares-refinement process either with a riding model or, in the case of H atoms attached to C atoms, located on special positions, fixed in place, with C—H = 0·95 Å. All non-H atoms were refined with anisotropic temperature factors and an overall isotropic temperature factor for the H atoms refined to 0·086 (8) Å^2. Full-matrix least-squares refinement converged rapidly (Table 1). On the final cycle of refinement no parameter of atom Cl(2) varied by more than $0{\cdot}024\sigma$ while the remaining parameters varied by no more than $0{\cdot}004\sigma$. On a final difference Fourier map the six largest features were within 1 Å of the Cu atom and varied from 0·38 to 0·73 e Å^{-3} in size. The residuals were identical for refinement of the model with the coordinates (xyz) replaced by ($\bar{x},\bar{y},\bar{z}$).

(6). In space group *Iba*2 the two Cu atoms of the $[Cu(pmdt)]_2(Bzim)^{3+}$ group are crystallographically independent. Their positions were determined from a Patterson synthesis and used for the initial phasing model. The remaining atoms were located using normal Fourier and difference Fourier maps. All of the H atoms of the pmdt ligand coordinated to Cu(2) were found on difference maps as were some of the H atoms of the Bzim group and the other pmdt ligand. All H atoms were placed in idealized geometric positions assuming C—H = 0·95 Å and allowed to ride on the C atom to which they were attached during least-squares refinement. Perchlorate groups one [Cl(1), O(11), O(12), O(13), O(14)] and three [Cl(3), O(31), O(32), O(33), O(34)] fully occupy general positions in the cell. Perchlorate group two [Cl(2), O(21), O(22)] occurs at position 4(*a*) and has C_2 site symmetry. Perchlorate group four is located at a general position but has only half-occupancy, in order to balance the charge. This partial occupancy was confirmed by the relative peak heights of atoms Cl(1), Cl(2), Cl(3) and Cl(4) on difference maps (9·8, 6·4, 7·5 and 3·2 e Å^{-3}, respectively) and also by the fact that the site-occupancy values for perchlorate groups two and three, when allowed to vary, refined to values of ~0·95. The O atom electron density about Cl(4) on difference or normal Fourier maps was confusing and consisted of five equally intense peaks located from ~1·1 to ~1·6 Å from Cl(4). It was impossible to assign any four of these peaks to the O atoms of a perchlorate group having acceptable geometry. Refinements with the atoms of this group constrained to reasonable positions using a variety of isotropic and anisotropic models were unsuccessful. Large temperature factors or poor shift-to-error values in the least-squares refinement were obtained. The problem was further complicated by the need to fill the approximately 5 to 6 Å diameter holes which are the results of the partial occupancy of this group. The chemical analysis and density of the crystals from which this crystal was chosen are consistent with there being eight water molecules in the unit cell. None of these appeared to be coordinated to the Cu atoms. Four water molecule atoms [O(*W*)] are located at positions 4(*b*). It is reasonable to expect that half of the eight general positions corresponding to perchlorate group four are filled with ClO_4^- groups, and that the remaining four positions are filled with water molecules. This model explains the fifth atom near atom Cl(4) and satisfies the water requirement. Deciding which of the five atoms [O(41), O(42), O(43), O(44), O(45)] is a water oxygen was not possible based on geometric considerations. In the final least-squares refinement the positions of the five O atoms were allowed to vary although the resulting geometry was chemically meaningless. The geometric parameters of the Cu coordination spheres and of the Cu—im—Cu unit, the determination of which was the purpose for studying the structure, were independent of the model chosen for this perchlorate group. During the final cycle of least-squares refinement, no parameters, except those associated with perchlorate group four, shifted by more than $0{\cdot}075\sigma$ and the average shift was $0{\cdot}013\sigma$. For perchlorate group four the maximum and minimum shifts were 0·35 and $0{\cdot}08\sigma$ respectively. Reflections 200, 110, 020 and 130 were not used in the refinement since, for these, $|F_o| << |F_c|$, possibly due to secondary extinction. Several aspects of the structure determination are substandard. The R factors are higher than one would expect considering the quality of the data. The geometry of the pmdt ligand attached to Cu(1) is uneven with C—N bond lengths as short as 1·40 Å and C—C bond lengths of 1·31–1·38 Å. Moreover, C- and N-atom temperature factors of this pmdt ligand are twice as large as those of the C and N atoms of the other pmdt ligand. Approximately 40 weak reflections ($|F_o| \sim 47$) have $|F_o| >> |F_c|$, with $\sum(|F_o| - |F_c|)/\sum|F_o| = 0{\cdot}72$ for these reflections. The most important features of the structure are the coordination geometry of the Cu atoms and the details of the Cu(1)—Bzim—Cu(2) bridging geometry. These details are in excellent agreement with expectations based on related structures. Furthermore, they showed no dependence on the range of data used in the refinement process. Least-squares refinements were carried out using all data, or using only data with $F_o \geq n\sigma(F_o)$ ($n = 1,2,3$), or using only data with $2\theta \leq 30°$. No Cu—N bond length or bond angle changed by more than $0{\cdot}5\sigma$, while R varied from 0·17 for all data to 0·055 for data with $2\theta \leq 30°$. In one trial refinement the bond lengths and angles of the poorly behaved pmdt ligand were constrained to reasonable values. With this model $R_1 = 0{\cdot}091$ and $R_2 = 0{\cdot}078$ (Table 1), a slight increase, but again the copper coordination and the Cu—Bzim—Cu geometries did not change significantly. Refinements using unit weights or data uncorrected for absorption also did not affect the important features of the structure. The higher thermal motion suggested by the larger thermal parameters of the Cu(1)—pmdt group may be real, since the Cu atom has no axial bonds and the unit-cell packing is not compact. Most likely there are unrecognized errors in the data that no adjustment of the refinement model can correct. These errors could be the result of twinning or some other problem with the data crystal (see above). Since the $[\mathrm{Cu(pmdt)}]_2\mathrm{Bzim}^{3+}$ geometry was satisfactorily determined, a more extensive search for better crystals was not undertaken.

Table 2. *Final non*-H *atom positional parameters and isotropic temperature factors for* (2)

Atoms are labeled as shown in Figs. 2 and 3. Numbers in parentheses are estimated uncertainties in the last significant digit(s). The origin is taken at the center of symmetry.

$$B_{\mathrm{eq}} = \tfrac{8}{3}\pi^2 \textstyle\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\mathrm{eq}}/B_{\mathrm{iso}}$(Å^2)
Cu(1)	0·05981 (3)	0·38030 (3)	0·35790 (7)	4·33 (3)
Cu(2)	0·14932 (3)	0·17193 (3)	0·30733 (7)	4·59 (3)
O(*W*1)	0·0331 (2)	0·3508 (2)	0·5057 (5)	8·3 (2)
O(*W*2)	0·0353 (8)	0·2398 (7)	0·5320 (11)	14·5 (8)
N(*T*1)	0·0994 (2)	0·4397 (2)	0·1610 (5)	5·0 (2)
O(11)	0·1122 (2)	0·4033 (2)	0·2051 (5)	6·9 (2)
O(12)	0·1202 (3)	0·4784 (2)	0·1755 (5)	10·8 (3)
O(13)	0·06565 (19)	0·4360 (2)	0·1034 (4)	6·2 (2)
N(*T*2)	0·1315 (4)	0·1439 (4)	0·5438 (11)	8·7 (5)
O(21)	0·1262 (7)	0·1432 (4)	0·6174 (8)	19·0 (8)
O(22)	0·1244 (5)	0·1761 (5)	0·4947 (10)	18·1 (6)
O(23)	0·1474 (5)	0·1113 (6)	0·5094 (12)	20·4 (8)
N(1)	0·0396 (2)	0·4541 (2)	0·3714 (4)	4·7 (2)
C(2*A*)	−0·0082 (5)	0·4655 (5)	0·3688 (12)	4·9 (3)
C(2*B*)	−0·0001 (7)	0·4714 (7)	0·3237 (17)	4·6 (4)
C(3*A*)	−0·0263 (6)	0·5113 (6)	0·3666 (14)	6·1 (4)
C(3*B*)	−0·0160 (7)	0·5197 (7)	0·3263 (16)	4·4 (4)
C(4)	0·0085 (4)	0·5508 (3)	0·3701 (8)	8·5 (4)
C(5*A*)	0·0558 (5)	0·5408 (5)	0·3737 (12)	4·9 (3)
C(5*B*)	0·0472 (8)	0·5347 (8)	0·429 (2)	6·6 (6)
C(6*A*)	0·0714 (5)	0·4929 (5)	0·3758 (12)	4·3 (3)
C(6*B*)	0·0627 (7)	0·4878 (7)	0·4220 (18)	5·0 (5)
C(7*A*)	0·1251 (4)	0·4825 (4)	0·3899 (9)	4·3 (3)
C(7*B*)	0·1060 (11)	0·4712 (11)	0·479 (2)	9·6 (8)
C(8)	0·1391 (3)	0·4435 (3)	0·4502 (8)	7·6 (3)
N(9)	0·1249 (2)	0·3960 (2)	0·4123 (5)	5·3 (2)
C(10)	0·1565 (3)	0·3613 (3)	0·4088 (6)	5·5 (3)
C(11)	0·1407 (2)	0·3159 (2)	0·3673 (6)	4·6 (2)
N(12)	0·09271 (17)	0·31514 (18)	0·3380 (4)	3·9 (2)
C(13)	0·0866 (2)	0·2698 (2)	0·3074 (5)	4·0 (2)
N(14)	0·12643 (18)	0·24137 (18)	0·3144 (4)	4·2 (2)
C(15)	0·1611 (2)	0·2714 (2)	0·3516 (6)	4·3 (2)
C(16)	0·2085 (2)	0·2488 (3)	0·3690 (6)	5·0 (2)
N(17)	0·21131 (18)	0·2033 (2)	0·3525 (5)	4·7 (2)
C(18)	0·2584 (2)	0·1778 (3)	0·3656 (7)	6·1 (3)
C(19)	0·2654 (2)	0·1399 (3)	0·2929 (6)	5·7 (3)
C(20)	0·2313 (3)	0·0967 (3)	0·2993 (6)	4·9 (2)
C(21)	0·2499 (3)	0·0496 (3)	0·3006 (7)	6·5 (3)
C(22)	0·2191 (4)	0·0105 (3)	0·3056 (7)	2·0 (1)
C(23)	0·1701 (3)	0·0177 (3)	0·3104 (7)	7·5 (3)
C(24)	0·1537 (3)	0·0647 (3)	0·3095 (6)	5·8 (3)
N(25)	0·18245 (19)	0·1042 (2)	0·3031 (4)	4·5 (2)
N(*I*1)	0·08218 (18)	0·15094 (17)	0·2773 (5)	4·1 (2)
C(*I*2)	0·0451 (2)	0·1475 (2)	0·3359 (6)	4·4 (2)
N(*I*3)	0·00200 (18)	0·13871 (18)	0·2978 (5)	4·1 (2)
C(*I*4)	0·0120 (2)	0·1370 (3)	0·2084 (6)	4·3 (2)
C(*I*5)	0·0606 (3)	0·1442 (2)	0·1957 (6)	4·5 (2)

Discussion. $[\mathrm{Cu}_2\mathit{bpim}(\mathit{im})]_2(\mathrm{NO}_3)_4.3\mathrm{H}_2\mathrm{O}$ (2). Positions of the atoms are reported in Table 2.* A listing of the bonds and angles is given in Table 3. The structure of the $[\mathrm{Cu_2bpim(im)}]_2^{4+}$ cation is shown in Fig. 2 along with the numbering scheme while Fig. 3 shows the Cu-atom coordination spheres.

The cation consists of $\mathrm{Cu_2bpim}^{3+}$ units (1, Fig. 1) linked through the Cu atoms *via* two bridging im ligands (Fig. 2) and related by a crystallographically required C_2 axis. A pseudomirror plane through C(13) and approximately perpendicular to the C(11)—C(15) bond bisects the $\mathrm{Cu_2bpim}^{3+}$ units. The four Cu atoms lie within ±0·36 Å of the best plane through them and

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* Lists of refined thermal parameters, observed and calculated structure-factor amplitudes, dihedral angle and mean-plane calculations (compounds 2 and 3), dihedral angle and best-plane calculations (5 and 6), H positional parameters (2, 5 and 6) and supplementary bonds and angles (2, 3 and 6) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38828 (63 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

form an approximate parallelogram of sides 6·214 (2) Å (within the Cu$_2$bpim^{3+} group) and 5·911 (2) Å (between the Cu$_2$bpim^{3+} groups). The dihedral angle made by the best planes through the two Cu$_2$bpim^{3+} groups is 153° and im rings which join these two units lie nearly perpendicular (86·5, 101·6°) to these groups.

The equatorial coordination sites of either Cu atom consist of three N atoms of the bpim ligand and one N atom of the im group which bridges the Cu$_2$bpim^{3+} halves. The axial sites of Cu(1) are occupied by a water molecule and an O atom of nitrate group one while those of Cu(2) are occupied by O atoms of two other nitrate groups (Fig. 3).

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *for* (2)

Atoms are labeled as in Figs. 2 and 3. E.s.d.'s, in parentheses, occur in the last significant figure for each parameter. Values reported have not been corrected for thermal motion.

Coordination spheres			
Cu(1)–N(1)	2·090 (5)	Cu(2)–N(25)	2·052 (5)
Cu(1)–N(9)	1·990 (5)	Cu(2)–N(17)	2·003 (5)
Cu(1)–N(12)	2·007 (5)	Cu(2)–N(14)	1·992 (5)
Cu(1)–N(*I*3$^{\rm i}$)	1·969 (5)	Cu(2)–N(*I*1)	1·964 (5)
Cu(1)–O(*W*1)	2·428 (7)	Cu(2)–O(22)	2·840 (14)
Cu(1)–O(11)	2·734 (6)	Cu(2)–O(13$^{\rm ii}$)	2·587 (6)
N(1)–Cu(1)–N(9)	89·5 (2)	N(25)–Cu(2)–N(17)	91·3 (2)
N(1)–Cu(1)–N(12)	168·3 (2)	N(25)–Cu(2)–N(14)	172·1 (2)
N(1)–Cu(1)–N(*I*3$^{\rm i}$)	94·0 (2)	N(25)–Cu(2)–N(*I*1)	98·1 (2)
N(9)–Cu(1)–N(12)	81·5 (2)	N(17)–Cu(2)–N(14)	80·9 (2)
N(9)–Cu(1)–N(*I*3$^{\rm i}$)	175·6 (2)	N(17)–Cu(2)–N(*I*1)	168·9 (2)
N(12)–Cu(1)–N(*I*3$^{\rm i}$)	94·8 (2)	N(14)–Cu(2)–N(*I*1)	89·8 (2)
O(*W*1)–Cu(1)–N(1)	98·9*	O(22)–Cu(2)–N(25)	99·8
O(*W*1)–Cu(1)–N(9)	88·7	O(22)–Cu(2)–N(17)	82·1
O(*W*1)–Cu(1)–N(12)	88·4	O(22)–Cu(2)–N(14)	80·6
O(*W*1)–Cu(1)–N(*I*3$^{\rm i}$)	93·4	O(22)–Cu(2)–N(*I*1)	90·5
O(11)–Cu(1)–N(1)	89·7	O(13$^{\rm ii}$)–Cu(2)–N(25)	85·4
O(11)–Cu(1)–N(9)	79·5	O(13$^{\rm ii}$)–Cu(2)–N(17)	85·6
O(11)–Cu(1)–N(12)	81·4	O(13$^{\rm ii}$)–Cu(2)–N(14)	92·5
O(11)–Cu(1)–N(*I*3$^{\rm i}$)	97·8	O(13$^{\rm ii}$)–Cu(2)–N(*I*1)	101·0
O(11)–Cu(1)–O(*W*1)	165·4	O(22)–Cu(2)–O(13)	166·7
im ring			
N(*I*1)–C(*I*2)	1·330 (8)	C(*I*2)–N(*I*3)	1·321 (8)
N(*I*1)–C(*I*5)	1·348 (9)	C(*I*4)–N(*I*3)	1·343 (9)
C(*I*4)–C(*I*5)	1·348 (9)		

bpim ligand	Position *A*	Position *B*		
N(1)–C(2)	1·336 (15)	1·37 (2)	N(25)–C(24)	1·332 (8)
C(2)–C(3)	1·34 (2)	1·39 (3)	C(24)–C(23)	1·356 (9)
C(3)–C(4)	1·432 (19)	1·25 (2)	C(23)–C(22)	1·347 (11)
C(4)–C(5)	1·316 (16)	1·44 (3)	C(22)–C(21)	1·356 (11)
C(5)–C(6)	1·371 (17)	1·35 (3)	C(21)–C(20)	1·377 (10)
C(6)–N(1)	1·369 (14)	1·34 (2)	C(20)–N(25)	1·346 (8)
C(6)–C(7)	1·503 (16)	1·51 (3)	C(20)–C(19)	1·501 (9)
C(7)–C(8)	1·433 (15)	1·25 (3)	C(19)–C(18)	1·498 (11)
C(8)–N(9)	1·459 (9)		C(18)–N(17)	1·469 (8)
N(9)–C(10)	1·276 (8)		N(17)–C(16)	1·263 (8)
C(10)–C(11)	1·445 (9)		C(16)–C(15)	1·452 (8)
C(11)–C(15)	1·351 (8)			
C(11)–N(12)	1·374 (7)		C(15)–N(14)	1·364 (8)
N(12)–C(13)	1·324 (8)		N(14)–C(13)	1·334 (7)

Non-bonded contacts			
Cu(1)–Cu(2)	6·2140 (22)	Cu(1)–Cu(2$^{\rm i}$)	5·9109 (22)
Cu(1)–Cu(2$^{\rm ii}$)	6·148 (2)	Cu(1)–Cu(2$^{\rm iii}$)	8·628 (2)

Symmetry code: (i) $-x, \frac{1}{2}-y, z$; (ii) $\frac{1}{4}-y, \frac{1}{4}+x, \frac{1}{4}-z$; (iii) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{1}{4}-z$.

* E.s.d.'s range from 0·2–0·3°.

The two crystallographically independent im groups are of two types. One of the im groups, called the *parallel* im ring, is part of the bpim ligand and is therefore constrained to lie nearly coplanar with the copper coordination planes in the Cu$_2$bpim^{3+} group. In contrast, the *perpendicular* im ring which bridges the two Cu$_2$bpim^{3+} halves makes angles of 97·3 and 100·0° with the coordination planes of the appended Cu atoms. Both types of im rings possess C_{2v} symmetry within experimental error and are planar to better than 0·006 Å.

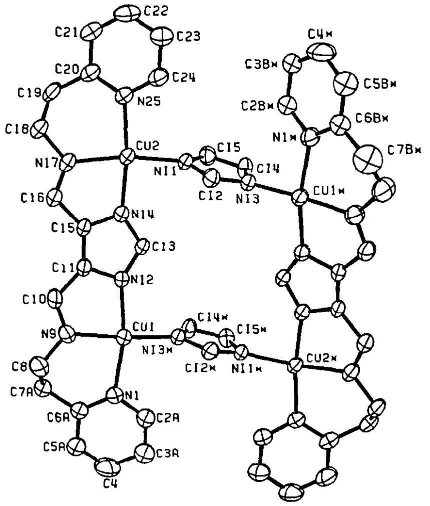

Fig. 2. View of the [Cu$_2$bpim(im)]$_2^{4+}$ cation showing the atom-labeling scheme. The view is approximately along the crystallographic $\bar{4}$ axis which passes through the center of the quadrilateral defined by atoms Cu(1), Cu(2), Cu(1*), Cu(2*) and which relates the starred and unstarred atoms. Atoms labeled *A* or *B* distinguish the two orientations of the disordered pyridine ring. The 35% probability thermal ellipsoids are depicted in this and all figures, except packing diagrams, in this paper. Atoms labeled *A* or *B* were refined isotropically. H atoms have been omitted for clarity in all figures except where noted.

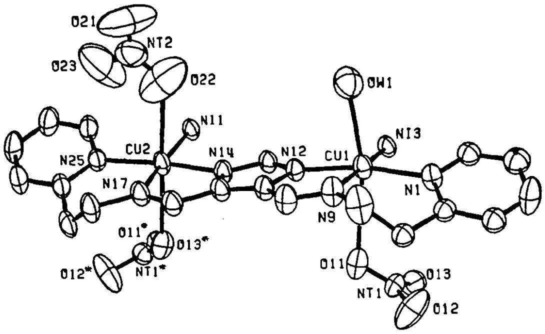

Fig. 3. View of the asymmetric unit of (2) showing the copper coordination geometry. Starred and unstarred atoms are related to each other by the crystallographic $\bar{4}$ axis. The lattice water molecule is not shown. See the caption to Fig. 2.

Table 4. *Final non-*H *atom positional parameters and isotropic temperature factors for* (3)

Atoms are labeled as in Figs. 4 and 5. Numbers in parentheses are the e.s.d.'s in the last significant digit(s). B_{eq} as defined in Table 2.

	x	y	z	B_{eq}/B_{iso}(Å^2)
Cu(1)	−0·37968 (17)	0·18416 (15)	0·03918 (11)	3·9 (1)
Cu(2)	−0·23865 (18)	0·43934 (14)	0·18875 (11)	3·7 (1)
Cu(3)	0·25739 (18)	0·45169 (14)	0·16690 (12)	4·0 (1)
Cu(4)	0·10997 (18)	0·20051 (15)	0·01135 (12)	3·9 (1)
*1A*N(1)	−0·3096 (10)	0·2388 (9)	0·1076 (7)	3·1 (4)
*1A*C(2)	−0·3211 (13)	0·3146 (12)	0·1152 (9)	3·4 (5)
*1A*N(3)	−0·2650 (10)	0·3325 (8)	0·1654 (7)	2·6 (4)
*1A*C(4)	−0·2224 (13)	0·2693 (12)	0·1928 (9)	3·6 (6)
*1A*C(5)	−0·2526 (12)	0·2093 (11)	0·1538 (8)	2·6 (5)
*1B*N(1)	0·2149 (10)	0·3507 (9)	0·1418 (7)	3·1 (4)
*1B*C(2)	0·1684 (12)	0·3347 (11)	0·0890 (8)	2·3 (5)
*1B*N(3)	0·1647 (10)	0·2568 (9)	0·0816 (7)	3·6 (4)
*1B*C(4)	0·2109 (13)	0·2276 (11)	0·1330 (9)	3·4 (6)
*1B*C(5)	0·2433 (13)	0·2848 (12)	0·1734 (9)	3·8 (6)
N(11)	−0·3043 (11)	0·1914 (11)	−0·0138 (7)	4·6 (5)
C(12)	−0·2561 (15)	0·2508 (13)	−0·0056 (10)	5·0 (6)
C(13)	−0·2094 (16)	0·2660 (15)	−0·0445 (12)	7·2 (8)
C(14)	−0·2127 (18)	0·2163 (17)	−0·0915 (12)	8·1 (8)
C(15)	−0·2618 (15)	0·1525 (14)	−0·0982 (10)	5·6 (6)
C(16)	−0·3098 (16)	0·1374 (14)	−0·0596 (11)	5·5 (6)
C(17)	−0·3610 (19)	0·0716 (16)	−0·0635 (11)	7·7 (8)
C(18)	−0·444 (2)	0·0922 (18)	−0·0726 (14)	9·6 (9)
N(19)	−0·4580 (13)	0·1204 (10)	−0·0216 (9)	5·5 (6)
C(110)	−0·5303 (16)	0·1082 (13)	−0·0132 (10)	5·4 (6)
C(111)	−0·5336 (16)	0·1385 (13)	0·0428 (11)	5·1 (6)
C(112)	−0·6061 (16)	0·1286 (14)	0·0629 (11)	6·3 (7)
C(113)	−0·5994 (16)	0·1544 (14)	0·1218 (11)	6·1 (7)
C(114)	−0·5318 (17)	0·1903 (14)	0·1578 (11)	6·3 (7)
C(115)	−0·4657 (14)	0·2002 (12)	0·1350 (10)	4·6 (6)
N(116)	−0·4706 (11)	0·1745 (10)	0·0800 (8)	4·7 (5)
N(21)	−0·3374 (11)	0·4559 (11)	0·2186 (7)	4·3 (5)
C(22)	−0·3662 (17)	0·3937 (14)	0·2408 (11)	6·2 (7)
C(23)	−0·4324 (17)	0·3972 (15)	0·2640 (11)	6·6 (7)
C(24)	−0·4668 (15)	0·4681 (14)	0·2661 (10)	5·3 (6)
C(25)	−0·4358 (16)	0·5299 (14)	0·2463 (10)	5·8 (6)
C(26)	−0·3727 (15)	0·5249 (13)	0·2201 (9)	4·4 (6)
C(27)	−0·3426 (16)	0·5943 (14)	0·1922 (10)	6·3 (7)
C(28)	−0·2561 (15)	0·6019 (13)	0·2198 (10)	5·0 (6)
N(29)	−0·2142 (11)	0·5487 (10)	0·1929 (8)	4·8 (5)
C(210)	−0·1597 (15)	0·5688 (14)	0·1658 (10)	5·6 (6)
C(211)	−0·1249 (14)	0·5109 (13)	0·1388 (9)	4·0 (6)
C(212)	−0·0667 (16)	0·5263 (14)	0·1090 (11)	6·2 (7)
C(213)	−0·0328 (17)	0·4683 (17)	0·0864 (12)	7·7 (8)
C(214)	−0·0599 (16)	0·3956 (14)	0·0933 (10)	6·2 (7)
C(215)	−0·1190 (16)	0·3788 (14)	0·1243 (10)	5·5 (6)
N(216)	−0·1476 (11)	0·4397 (11)	0·1466 (7)	4·4 (5)
N(31)	0·1705 (11)	0·4816 (10)	0·2057 (7)	4·2 (5)
C(32)	0·1281 (14)	0·4266 (12)	0·2237 (9)	3·8 (6)
C(33)	0·0659 (14)	0·4428 (14)	0·2489 (10)	4·8 (6)
C(34)	0·0501 (16)	0·5180 (15)	0·2580 (10)	6·1 (7)
C(35)	0·0916 (15)	0·5744 (13)	0·2399 (9)	4·7 (6)
C(36)	0·1543 (13)	0·5570 (13)	0·2143 (9)	3·6 (5)
C(37)	0·1977 (16)	0·6137 (13)	0·1921 (10)	5·7 (6)
C(38)	0·2902 (17)	0·6098 (15)	0·2106 (11)	6·7 (7)
N(39)	0·3131 (14)	0·5531 (13)	0·1806 (10)	7·9 (6)
C(310)	0·3677 (17)	0·5659 (15)	0·1519 (11)	7·0 (7)
C(311)	0·3899 (15)	0·5012 (14)	0·1245 (10)	4·4 (6)
C(312)	0·4532 (14)	0·5045 (13)	0·0994 (9)	4·4 (6)
C(313)	0·4726 (14)	0·4408 (14)	0·0742 (9)	5·0 (6)
C(314)	0·4323 (19)	0·3701 (16)	0·0735 (12)	8·0 (8)
C(315)	0·3702 (18)	0·3772 (16)	0·1030 (12)	7·1 (8)
N(316)	0·3498 (11)	0·4353 (12)	0·1269 (8)	5·1 (5)
N(41)	0·1944 (11)	0·2201 (11)	−0·0340 (7)	4·4 (5)
C(42)	0·2283 (15)	0·2905 (14)	−0·0281 (10)	5·3 (6)
C(43)	0·2858 (16)	0·3060 (15)	−0·0567 (11)	6·4 (7)
C(44)	0·3082 (16)	0·2513 (17)	0·9089 (11)	7·3 (8)
C(45)	0·2701 (16)	0·1832 (14)	−0·1011 (10)	5·9 (6)
C(46)	0·2125 (14)	0·1648 (13)	−0·0710 (10)	4·4 (6)
C(47)	0·1696 (15)	0·0907 (13)	−0·0812 (9)	4·9 (6)
C(48)	0·0780 (14)	0·1041 (12)	−0·1019 (9)	4·2 (6)
N(49)	0·0556 (11)	0·1241 (9)	−0·0490 (7)	3·6 (4)
C(410)	−0·0075 (14)	0·0940 (11)	−0·0395 (9)	3·6 (6)
C(411)	−0·0297 (14)	0·1188 (12)	0·0117 (10)	3·9 (6)
C(412)	−0·0974 (14)	0·0895 (12)	0·0277 (10)	4·3 (6)
C(413)	−0·1116 (14)	0·1159 (12)	0·0792 (10)	4·5 (6)
C(414)	−0·0593 (14)	0·1674 (12)	0·1180 (9)	4·3 (6)
C(415)	0·0067 (14)	0·1923 (12)	0·0986 (10)	4·7 (6)
N(416)	0·0180 (10)	0·1684 (9)	0·0477 (8)	3·9 (4)
O(*W*1)	−0·4433 (9)	0·3042 (8)	−0·0119 (6)	4·9 (4)
O(*W*2)	0·1745 (9)	0·5076 (8)	0·0647 (6)	4·8 (4)
O(*W*3)	0·3401 (9)	0·4087 (8)	0·2635 (6)	5·0 (4)
O(*W*4)	−0·0765 (10)	0·2902 (9)	0·3198 (7)	7·2 (5)
O(*W*5)	−0·1596 (9)	0·4180 (8)	0·2818 (6)	5·9 (4)
N(*T*11)*	−0·332 (2)	0·0203 (16)	0·1201 (13)	9·4 (8)
N(*T*12)	−0·3173 (11)	0·0593 (10)	0·0806 (8)	7·5 (5)
N(*T*13)	−0·2707 (14)	0·0144 (11)	0·1613 (9)	9·9 (6)
N(*T*14)	−0·3916 (18)	0·0121 (15)	0·1274 (12)	14·5 (9)
N(*T*21)	−0·3063 (14)	0·4740 (13)	0·0287 (10)	6·2 (6)
N(*T*22)	−0·3411 (11)	0·4852 (10)	0·0659 (8)	7·6 (5)
N(*T*23)	−0·3183 (10)	0·4162 (10)	−0·0005 (7)	6·9 (5)
N(*T*24)	−0·2594 (11)	0·5206 (9)	0·0185 (7)	6·3 (5)
N(*T*31)	0·9829 (19)	0·3305 (18)	0·9492 (13)	7·3 (7)
N(*T*32)	0·951 (3)	0·387 (2)	0·947 (2)	9 (2)
N(*T*33)	0·958 (4)	0·272 (4)	0·925 (2)	15 (2)
N(*T*34)	0·048 (3)	0·316 (3)	0·980 (2)	12 (2)
N(*T*35)	0·998 (3)	0·375 (3)	0·993 (3)	9 (2)
N(*T*36)	0·033 (4)	0·290 (3)	0·941 (3)	9 (2)
N(*T*37)	0·920 (3)	0·355 (3)	0·905 (3)	10 (2)
N(*T*41)	−0·1905 (18)	−0·4643 (14)	0·3968 (13)	9·0 (8)
N(*T*42)	−0·1974 (12)	−0·4365 (11)	0·4404 (9)	9·5 (6)
N(*T*43)	−0·1322 (16)	−0·4830 (13)	0·3790 (11)	13·3 (8)
N(*T*44)	−0·2586 (11)	−0·4660 (9)	0·3550 (7)	6·6 (5)
N(*T*51)	−0·524 (2)	0·2585 (17)	−0·1744 (17)	8·1 (8)
N(*T*52)	−0·500 (2)	0·301 (2)	−0·1279 (18)	3 (2)
N(*T*53)	−0·492 (3)	0·278 (3)	−0·214 (2)	5 (2)
N(*T*54)	−0·560 (3)	0·204 (3)	−0·163 (3)	6 (2)
N(*T*55)	−0·572 (2)	0·2316 (18)	−0·2146 (17)	8 (1)
N(*T*56)	−0·460 (3)	0·283 (3)	−0·174 (3)	16 (2)
N(*T*57)	−0·521 (4)	0·248 (4)	−0·126 (3)	22 (3)
N(*T*61)	0·076 (2)	0·239 (2)	0·2600 (17)	13 (1)
N(*T*62)	−0·0025 (14)	0·2594 (12)	0·2360 (9)	10·2 (6)
N(*T*63)	0·0789 (19)	0·1843 (19)	0·2340 (13)	18 (1)
N(*T*64)	0·0807 (17)	0·2382 (16)	0·3103 (12)	16 (1)

* Nitrate-group atoms are designated N(*T*). The first number in the atom label indicates to which nitrate group (one through six) the atom belongs.

All of the other geometric features of the Cu$_2$bpim^{3+} group are normal and there is very good agreement between equivalent bond distances and angles in each half of the ligand. The asymmetry observed in the bond lengths associated with atoms N(1) and C(4) suggests that the two positions of these atoms associated with the two orientations of the pyridine ring are not exactly the same. The short C(7*A*)–C(8) distance probably indicates disorder of atom C(8) which has not been included in the model.

The nitrate groups are planar to within 0·005 Å. No non-H atom–atom contacts of less than 3·1 Å (other than those already noted) are observed. Crystal packing is discussed in Kolks (1980).

[Cu(*pip*)]$_2$(*im*)(NO$_3$)$_3$.2·5H$_2$O (3). Table 4 lists the atom positions and Table 5 summarizes the copper-coordination-sphere geometry and average structural data for the pip ligand and the nitrate groups. Fig. 4 shows the [Cu$_2$(pip)]$_2$(im)$^{3+}$ geometry and atom-labeling scheme and the copper coordination spheres are shown in Fig. 5.

The crystallographic asymmetric unit consists of two cations (Fig. 4), six nitrate groups and five water molecules, four of which are coordinated to the Cu atoms. The axial sites of each Cu atom are occupied by either water molecules or the O atoms of the nitrate groups [Cu–O(water) 2·281 (15) – 2·643 (13) Å, Cu–O(nitrate) 2·35 (5) – 3·07 Å] (Fig. 5). It is interesting that the copper coordination geometries of the four Cu(pip)$^{2+}$ units are virtually identical to those of the Cu atoms in (1) and (2).

Both im rings are planar to better than 0·02 Å and lie approximately perpendicular to the copper coordination planes of the appended Cu atoms. The im ring *A* makes angles of 95 and 80·1° with the coordination planes of atoms Cu(1) and Cu(2) while im ring *B* makes angles of 90·0 and 77·4° with the planes of atoms Cu(3) and Cu(4).

Table 5. *Selected interatomic distances* (Å) *and angles* (°) *for* (3)

Atoms are labeled as in Figs. 4 and 5. E.s.d.'s, in parentheses, occur in the last significant figure for each parameter. Values reported have not been corrected for thermal motion.

Copper equatorial planes

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	av.[a]
Cu—N(1)	2·05 (2)	2·05 (2)	2·05 (2)	2·07 (2)	2·06 (1)
Cu—N(9)	2·036 (18)	1·990 (18)	2·03 (2)	2·009 (16)	2·02 (1)
Cu—N(16)	2·08 (2)	2·09 (2)	2·10 (2)	2·10 (2)	2·09 (1)
Cu—*I*N	1·992 (15)	1·999 (15)	1·974 (15)	1·947 (16)	1·978 (12)
N(1)—Cu—N(9)	91·5 (8)	91·8 (8)	94·5 (9)	90·8 (8)	92·2 (8)
N(1)—Cu—*I*N	96·2 (7)	94·5 (7)	96·2 (8)	95·6 (7)	95·6 (4)
N(1)—Cu—N(16)	170·6 (6)	168·6 (7)	172·9 (8)	171·5 (7)	170·9 (5)
N(9)—Cu—N(16)	80·1 (8)	80·8 (8)	78·6 (9)	80·7 (7)	80·1 (5)
N(9)—Cu—*I*N	171·3 (8)	167·2 (7)	168·7 (9)	167·8 (7)	168·8 (9)
N(16)—Cu—*I*N	92·5 (7)	91·1 (7)	90·6 (8)	92·7 (7)	91·7 (5)

Copper axial sites

Cu(1)—O(*W*1)	2·554 (14)	Cu(1)—N(*T*12)	2·550 (18)
Cu(2)—O(*W*5)	2·281 (13)	Cu(2)—N(*T*22)	3·07
Cu(3)—O(*W*3)	2·461 (13)	Cu(3)—O(*W*2)	2·643 (13)
Cu(4)—N(*T*34)	2·35 (5)	Cu(4)—N(*T*36)	2·43 (5)
Cu(4)—N(*T*42^{i})	2·94 (3)		
O(*W*1)—Cu(1)—N(11)	86·0 (6)	N(*T*12)—Cu(1)—N(11)	90·5 (7)
O(*W*1)—Cu(1)—N(19)	90·7 (6)	N(*T*12)—Cu(1)—N(19)	85·3 (6)
O(*W*1)—Cu(1)—N(116)	89·9 (6)	N(*T*12)—Cu(1)—N(116)	93·0 (7)
O(*W*1)—Cu(1)—*IA*N(1)	93·7 (5)	N(*T*12)—Cu(1)—*IA*N(1)	90·7 (6)
O(*W*1)—Cu(1)—N(*T*12)	174·6 (5)	O(*W*5)—Cu(2)—N(216)	96·7 (6)
O(*W*5)—Cu(2)—N(21)	92·3 (6)	O(*W*5)—Cu(2)—*IA*N(3)	98·0 (6)
O(*W*5)—Cu(2)—N(29)	92·9 (6)	O(*W*2)—Cu(3)—N(31)	91·2 (6)
O(*W*3)—Cu(3)—N(31)	89·3 (6)	O(*W*2)—Cu(3)—N(39)	86·0 (7)
O(*W*3)—Cu(3)—N(39)	89·7 (7)	O(*W*2)—Cu(3)—N(316)	86·6 (6)
O(*W*3)—Cu(3)—N(16)	92·4 (6)	O(*W*2)—Cu(3)—*IB*N(3)	90·1 (5)
O(*W*3)—Cu(3)—*IB*N(1)	94·1 (5)	N(*T*36)—Cu(4)—N(41)	82·7 (18)
O(*W*3)—Cu(3)—O(*W*2)	175·7 (5)	N(*T*36)—Cu(4)—N(49)	83·8 (14)
N(*T*34)—Cu(4)—N(41)	91·4 (17)	N(*T*36)—Cu(4)—N(416)	96·8 (18)
N(*T*34)—Cu(4)—N(49)	106·6 (13)	N(*T*36)—Cu(4)—*IB*N(3)	107·3 (14)
N(*T*34)—Cu(4)—N(416)	91·5 (16)	N(*T*34)—Cu(4)—N(*T*36	24·5 (19)
N(*T*34)—Cu(4)—*IB*N(3)	83·7 (13)		

im ring

*IA*N(1)—*IA*C(2)	1·38 (3)	*IB*N(1)—*IB*C(2)	1·32 (2)
*IA*C(2)—*IA*N(3)	1·35 (2)	*IB*C(2)—*IB*N(3)	1·40 (3)
*IA*N(3)—*IA*C(4)	1·41 (3)	*IB*N(3)—*IB*C(4)	1·36 (2)
*IA*C(4)—*IA*C(5)	1·41 (3)	*IB*C(4)—*IB*C(5)	1·40 (3)
*IA*C(5)—*IA*N(1)	1·36 (2)	*IB*C(5)—*IB*N(1)	1·41 (3)

pip ligand[b]

N(1)—C(2)	1·37 (1)	N(9)—C(10)	1·33 (1)
C(2)—C(3)	1·40 (1)	C(10)—C(11)	1·43 (1)
C(3)—C(4)	1·40 (1)	C(11)—C(12)	1·43 (2)
C(4)—C(5)	1·38 (1)	C(12)—C(13)	1·39 (2)
C(5)—C(6)	1·42 (1)	C(13)—C(14)	1·42 (1)
C(6)—N(1)	1·41 (1)	C(14)—C(15)	1·43 (1)
C(6)—C(7)	1·49 (3)	C(15)—N(16)	1·34 (2)
C(7)—C(8)	1·51 (3)	N(16)—C(11)	1·37 (1)
C(8)—N(9)	1·41 (2)		

(*a*) The number in parentheses is *s*, the standard deviation of the mean $\{=[\sum^n (x_i - \bar{x})^2/n(n-1)]^{1/2}\}$.

(*b*) Average values and standard deviations of the mean for four independent pip ligands. The e.s.d.'s for the individual bond lengths are ~0·04 Å and ~2° for the bond angles.

Symmetry code: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Intracation hydrogen-bonding interactions are shown in Fig. 5. The dimensions of the nitrate groups are reasonable, the deviations from D_{3h} symmetry and 1·24 Å N—O bond lengths being a function of the amount of disorder in the particular group and how securely it is held in the lattice. Crystal packing is discussed in Kolks (1980).

[Cu(*pmdt*)]$_2$(2-*Meim*)(ClO$_4$)$_3$ (5). A listing of the final atom coordinates is given in Table 6 and bond lengths and angles are in Table 7. Fig. 6 shows the [Cu(pmdt)]$_2$(2-Meim)$^{3+}$ cation along with the numbering scheme and Fig. 7 shows the packing scheme of the unit cell.

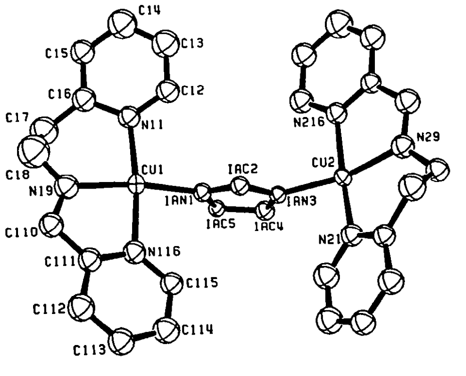

Fig. 4. Drawing of one of the two [Cu(pip)]$_2$(im)$^{3+}$ moieties which constitute the crystallographic asymmetric unit in compound (3). The first number in the pip-ligand atom label denotes to which Cu atom (1 to 4) the ligand is coordinated. The next digit(s) (numbers 1 to 16) indicate the position of the atom in the pip ligand. The atoms of the two im rings are prefixed by the letters *IA* or *IB*. See the caption to Fig. 2.

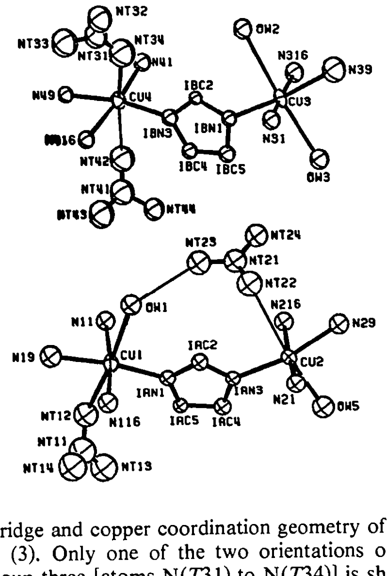

Fig. 5. im bridge and copper coordination geometry of the four Cu atoms in (3). Only one of the two orientations of disordered nitrate group three [atoms N(*T*31) to N(*T*34)] is shown. Atoms O(*W*1) and N(*T*23) are weakly hydrogen-bonded [O(*W*)—N(*T*23) 2·91 Å]. See the caption to Fig. 2.

The cation consists of two $\mathrm{Cu(pmdt)^{2+}}$ groups bridged by a 2-Meim anion (Fig. 6). It has crystallographically required *mm* symmetry with one mirror plane coplanar with the im ring and the other plane bisecting the im ring.

The coordination sphere of the Cu atom consists of three N atoms of the pmdt ligand and one N atom of the im ring. The two copper coordination planes make a dihedral angle of 112·9° while the Cu—N(im) vectors intersect at an angle of 127·5°. The methyl groups of the 2-Meim ring and atom N(6) block one axial site of the Cu atom while the sixth site is occupied by the unique methyl group, C(7), of a $\mathrm{Cu(pmdt)^{2+}}$ group from the adjacent unit cell along **c** (Fig. 7).

The geometry of the 2-Meim ring is normal. The movement of the Cu atoms toward the methyl group is manifest by the Cu—N(*I*)—C(2*I*) angle of 133·8 (7)°, the Cu—N(*I*)—C(3*I*) angle of 120·6 (8)° and the Cu···Cu* distance of 5·6621 (17) Å. It is noteworthy that the distortion of the Cu atoms is *toward* the methyl group, the opposite of what would be expected and what, in fact, has been predicted (Haddad & Hendrickson, 1978) for related systems.

The cations lie at the corners and center of a body-centered cell with the Cu···Cu* vectors directed along the *a* axis and with the Cu—2Meim—Cu units lying on the mirror planes perpendicular to **b** (Fig. 7). The two perchlorate groups are located in pockets that exist between the tightly packed cations. The shortest Cu—O(perchlorate) distance is 4·54 Å and there are no unusually short intermolecular distances.

As indicated in the *Experimental*, there was crystallographic evidence that compound (5) is partially ordered in a lower-symmetry space group. A discussion of possible models is given elsewhere (Kolks, 1980).

Table 6. *Final non-*H *atom positional parameters and equivalent isotropic thermal factors for* (5)

Atoms are labeled as in Fig. 6. Numbers in parentheses are estimated uncertainties in the last significant digit(s). B_{eq} as defined in Table 2.

	x	y	z	B_{eq}(Å^2)
Cu	0·19900 (6)	0·0000	0·2500	4·37 (3)
N(1)	0·2239 (4)	0·1241 (4)	0·2780 (12)	5·9 (2)
C(2)	0·1415 (5)	0·1796 (4)	0·2731 (17	7·4(3)
C(3)	0·2696 (8)	0·1315 (7)	0·4433 (12)	8·3 (5)
C(4)	0·2910 (7)	0·1444 (7)	0·1416 (14)	7·6 (4)
C(5)	0·3579 (5)	0·0755 (6)	0·1128 (13)	7·1 (3)
N(6)	0·3013 (5)	0·0000	0·0844 (12)	5·5 (3)
C(7)	0·2560 (8)	0·0000	−0·0836 (15)	7·5 (5)
N(*I*)	0·0778 (5)	0·0000	0·3567 (11)	5·0 (3)
C(2*I*)	0·0485 (7)	0·0000	0·5214 (13)	5·5 (4)
C(4*I*)	0·0000	0·0000	0·074 (2)	5·7 (5)
C(3*I*)	0·0000	0·0000	0·266 (2)	4·0 (4)
Cl(1)	0·0000	−0·20701 (18)	0·7862 (4)	5·7 (1)
O(11)	0·0000	−0·2748 (9)	0·890 (2)	12·0 (7)
O(12)	−0·0812 (4)	−0·1608 (4)	0·8155 (9)	8·8 (3)
O(13)	0·0000	−0·2339 (10)	0·6239 (16)	11·9 (7)
Cl(2)	0·5000	−0·015 (4)	−0·3606 (10)	12 (2)
O(21)	0·5000	0·049 (3)	−0·265 (4)	16 (2)
O(22)	0·5000	0·0000	−0·531 (2)	15 (1)
O(23)	0·4267 (12)	−0·064 (2)	−0·337 (3)	23 (2)

Table 7. *Interatomic distances* (Å) *and angles* (°) *for* (5)

Atoms are labeled as in Fig. 6. E.s.d.'s, in parentheses, occur in the last significant figure for each parameter. Values have not been corrected for thermal motion.

Cu—N(1)	2·055 (6)	N(1)—C(2)	1·479 (8)
Cu—N(6)	1·964 (8)	N(1)—C(3)	1·474 (13)
Cu—N(*I*)	1·923 (7)	N(1)—C(4)	1·484 (13)
N(*I*) C(2*I*)	1·377 (13)	C(4)—C(5)	1·485 (13)
N(*I*)—C(3*I*)	1·322 (12)	C(5)—N(6)	1·483 (8)
C(2*I*)—C(2*I*^{i})	1·381 (19)	N(6)—C(7)	1·487 (15)
C(3*I*)—C(4*I*)	1·53 (3)	Cl(2) O(21)	1·30 (7)
Cl(1)—O(11)	1·374 (12)	Cl(2) O(22)	1·38 (3)
Cl(1)—O(12)	1·396 (6)	Cl(2)—O(23)	1·32 (5)
Cl(1)—O(13)	1·365 (13)	Cu···Cu^{i}	5·6619 (7)
N(1)—Cu—N(6)	86·9 (2)	N(*I*) Cu—N(1)	96·1 (2)
N(*I*)—Cu—N(6)	164·0 (3)	N(1) Cu—N(1^{ii})	156·5 (3)
Cu—N(*I*) C(2*I*)	133·8 (7)	N(*I*)—C(2*I*)—C(2*I*^{i})	107·6 (9)
Cu—N(*I*)—C(3*I*)	120·6 (8)	N(*I*)—C(3*I*)—N(*I*^{i})	113·7 (14)
C(2*I*)—N(*I*)—C(3*I*)	105·6 (9)	N(*I*)—C(3*I*)—C(4*I*)	123·2 (7)
Cu—N(1)—C(2)	117·1 (4)	N(1)—C(4)—C(5)	111·0 (8)
Cu—N(1)—C(3)	104·7 (6)	C(4)—C(5)—N(6)	107·3 (6)
Cu—N(1)—C(4)	104·4 (6)	C(5)—N(6)—C(7)	111·9 (6)
C(2)—N(1)—C(3)	108·9 (9)	C(5)—N(6)—C(5^{ii})	111·3 (6)
C(2)—N(1)—C(4)	110·8 (9)	Cu—N(6)—C(5)	107·5 (5)
C(3)—N(1)—C(4)	110·7 (7)	Cu—N(6)—C(7)	106·5 (6)
O(11)—Cl—O(12)	109·2 (7)	O(21)—Cl(2)—O(22)	116 (5)
O(12)—Cl(1)—O(12^{i})	111·6 (5)	O(21)—Cl(2)—O(23)	113·5 (15)
O(11)—Cl(1)—O(13)	108·2 (9)	O(22)—Cl(2)—O(23)	104·2 (18)
O(12) Cl(1)—O(13)	109·2 (5)	O(23)—Cl(2) O(23^{i})	104 (5)

Symmetry code: (i) $-x, y, z$; (ii) $x, -y, z$.

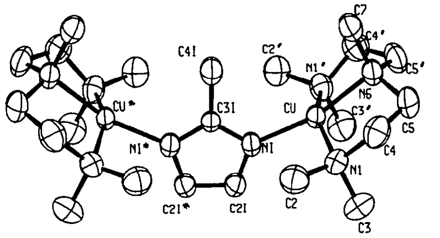

Fig. 6. View of the $\mathrm{[Cu(pmdt)]_2(2\text{-}Meim)^{3+}}$ cluster of compound (5) showing the atom-labeling scheme. Crystallographically required mirror planes, one lying in the plane of the im ring and one perpendicular to and bisecting the C(2*I*)—C(2*I**) bond, relate the primed to the unprimed and the starred to the unstarred atoms, respectively. See the caption to Fig. 2.

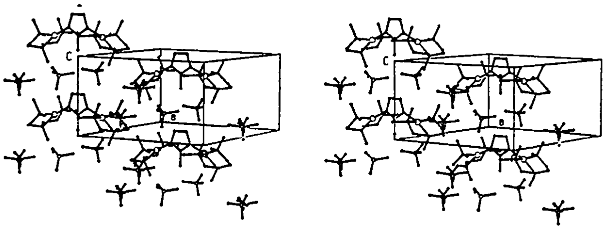

Fig. 7. Stereodrawing showing the packing of the contents of two unit cells of (5). Four extra $\mathrm{ClO_4^-}$(II) groups have been included. Both orientations of this disordered anion are shown. Atoms are shown as spheres of arbitrary size.

The present treatment of the data gives chemically reasonable results and is deemed to be sufficient for our purposes.

[Cu(*pmdt*)]$_2$(*Bzim*)(ClO$_4$)$_3$.H$_2$O (6). Final positional parameters may be found in Table 8, the results of the bonds and angles calculations in Table 9. Fig. 8 shows the [Cu(pmdt)]$_2$(ClO$_4$)(Bzim)$^{2+}$ cation and Fig. 9 the unit-cell contents.

The cation is composed of two Cu(pmdt)$^{2+}$ groups bridged by a Bzim ligand; a perchlorate group is also coordinated to one of the Cu atoms (Fig. 8). The symmetry is nearly C_s with the mirror lying in the plane of the Bzim ring.

Table 8. *Final non-*H *atom positional parameters and isotropic temperature factors for* (6)

Atoms are labeled as in Fig. 8. Numbers in parentheses are estimated uncertainties in the last significant digit(s). B_{eq} as defined in Table 2.

	x	y	z	B_{eq}/B_{iso}(Å^2)
Cu(1)	0·19259 (15)	0·32843 (7)	0·1600	3·86 (7)
Cu(2)	0·31665 (14)	0·40400 (6)	0·5400 (3)	3·04 (6)
Cl(1)	0·1836 (5)	0·3346 (2)	0·6341 (7)	6·6 (3)
O(11)	0·1319 (13)	0·3528 (8)	0·706 (2)	13 (1)
O(12)	0·2319 (11)	0·3595 (5)	0·5918 (14)	7·8 (7)
O(13)	0·2291 (18)	0·3098 (6)	0·698 (3)	15 (1)
O(14)	0·1452 (13)	0·3169 (6)	0·557 (2)	13 (1)
Cl(2)	0·5000	0·5000	0·4418 (6)	2·8 (2)
O(21)	0·4539 (11)	0·5225 (5)	0·3797 (17)	8·5 (7)
O(22)	0·4523 (9)	0·4789 (4)	0·5059 (13)	6·1 (5)
Cl(3)	0·0549 (6)	0·2187 (3)	0·3370 (8)	8·1 (3)
O(31)	0·075 (3)	0·1860 (8)	0·364 (3)	21 (2)
O(32)	0·1219 (17)	0·2393 (9)	0·328 (3)	18 (2)
O(33)	0·042 (2)	0·2187 (11)	0·234 (3)	19 (2)
O(34)	0·014 (3)	0·2325 (8)	0·405 (4)	24 (2)
Cl(4)	−0·0850 (16)	0·4426 (7)	0·415 (2)	12 (1)
O(41)	−0·088 (4)	0·470 (2)	0·368 (8)	18 (3)
O(42)	−0·134 (3)	0·4094 (18)	0·399 (6)	16 (2)
O(43)	−0·023 (5)	0·434 (2)	0·430 (8)	21 (3)
O(44)	−0·071 (4)	0·4688 (19)	0·516 (7)	18 (3)
O(45)	−0·058 (4)	0·449 (2)	0·304 (7)	17 (2)
O(*W*)	0·0000	0·5000	0·116 (9)	19 (3)
N(11)	0·2865 (11)	0·2957 (5)	0·157 (2)	6·5 (5)
C(12)	0·3587 (15)	0·3116 (8)	0·147 (3)	9·8 (9)
C(13)	0·2875 (15)	0·2753 (7)	0·255 (2)	7·4 (8)
C(14)	0·2656 (18)	0·2695 (8)	0·063 (3)	9·6 (9)
C(15)	0·1913 (15)	0·2657 (7)	0·056 (3)	7·6 (7)
N(16)	0·1498 (11)	0·2978 (5)	0·043 (2)	6·2 (5)
C(17)	0·1655 (18)	0·3134 (8)	−0·064 (3)	11 (1)
C(18)	0·0682 (18)	0·2954 (9)	0·063 (3)	12 (1)
C(19)	0·0394 (19)	0·3282 (9)	0·091 (3)	12 (1)
N(110)	0·0843 (13)	0·3471 (7)	0·180 (2)	9·1 (6)
C(111)	0·0767 (16)	0·3842 (8)	0·187 (3)	9·8 (9)
C(112)	0·0637 (18)	0·3309 (9)	0·284 (3)	9·6 (9)
N(21)	0·2368 (9)	0·4452 (4)	0·5442 (18)	4·5 (4)
C(22)	0·1571 (12)	0·4343 (6)	0·515 (2)	5·8 (6)
C(23)	0·2607 (12)	0·4746 (6)	0·4765 (18)	5·0 (6)
C(24)	0·2375 (11)	0·4579 (6)	0·659 (2)	5·5 (6)
C(25)	0·3201 (11)	0·4555 (5)	0·7016 (19)	5·2 (6)
N(26)	0·3442 (8)	0·4182 (4)	0·6930 (13)	3·2 (3)
C(27)	0·3103 (14)	0·3950 (7)	0·778 (2)	5·5 (6)
C(28)	0·4279 (9)	0·4157 (4)	0·6952 (15)	2·7 (4)
C(29)	0·4511 (11)	0·3798 (5)	0·6527 (19)	4·1 (5)
N(210)	0·4178 (7)	0·3742 (4)	0·5458 (15)	2·9 (3)
C(211)	0·4047 (12)	0·3356 (5)	0·5241 (20)	4·9 (6)
C(212)	0·4724 (10)	0·3872 (5)	0·4621 (16)	3·9 (5)
N(1)	0·2437 (9)	0·3642 (4)	0·2454 (13)	3·4 (3)
C(2)	0·2512 (13)	0·3653 (6)	0·3559 (19)	3·9 (4)
N(3)	0·2953 (9)	0·3931 (4)	0·3872 (13)	3·6 (4)
C(4)	0·3210 (11)	0·4098 (5)	0·2929 (15)	2·9 (4)
C(5)	0·3689 (11)	0·4388 (5)	0·2744 (17)	3·4 (5)
C(6)	0·3806 (10)	0·4492 (5)	0·1753 (18)	3·9 (5)
C(7)	0·3452 (12)	0·4322 (6)	0·0837 (18)	4·3 (6)
C(8)	0·2981 (12)	0·4050 (6)	0·1024 (19)	4·3 (6)
C(9)	0·2863 (11)	0·3929 (5)	0·2095 (16)	3·3 (5)

The equatorial coordination plane of each Cu atom consists of three N atoms of the pmdt ligand and one N atom of the Bzim group (Fig. 8). It is noteworthy that, unlike [Cu(pmdt)]$_2$(im)(ClO$_4$)$_3$ (O'Young *et al.*, 1978) and [Cu(pmdt)]$_2$(2-Meim)(ClO$_4$)$_3$, the methyl groups on atoms N(15) and N(26) of the pmdt ligands lie on opposite sides of the plane defined by atoms N(11), N(110), N(21) and N(210).

Table 9. *Selected interatomic distances* (Å) *and angles* (°) *for* (6)

Atoms are labeled as in Fig. 8. E.s.d.'s, in parentheses, occur in the last significant figure for each parameter. Values have not been corrected for thermal motion. Geometry for the disordered perchlorate groups may be found in Kolks (1980).

Coordination spheres			
Cu(1)–N(11)	2·046 (19)	Cu(2)–N(21)	2·081 (16)
Cu(1)–N(16)	2·00 (2)	Cu(2)–N(26)	2·039 (16)
Cu(1)–N(110)	2·03 (2)	Cu(2)–N(210)	2·090 (13)
Cu(1)–N(1)	1·930 (16)	Cu(2)–N(3)	1·984 (17)
		Cu(2)–O(12)	2·321 (17)
N(11)–Cu(1)–N(16)	86·6 (8)	N(21)–Cu(2)–N(26)	86·5 (7)
N(11)–Cu(1)–N(110)	162·5 (9)	N(21)–Cu(2)–N(210)	164·0 (6)
N(11)–Cu(1)–N(1)	93·3 (8)	N(21)–Cu(21)–N(3)	93·0 (8)
N(16)–Cu(1)–N(110)	86·6 (9)	N(21)–Cu(2)–O(12)	95·8(7)
N(16)–Cu(1)–N(1)	166·6 (8)	N(26)–Cu(2)–N(210)	84·7 (6)
N(110)–Cu(1)–N(1)	97·0 (9)	N(26)–Cu(2)–N(3)	175·6 (7)
N(210)–Cu(2)–O(12)	98·2 (6)	N(26)–Cu(2)–O(12)	94·4 (6)
N(3)–Cu(2)–O(12)	89·9 (6)	N(210)–Cu(2)–N(3)	94·7 (6)
Bzim group			
N(1)–C(2)	1·38 (2)	C(5)–C(6)	1·31 (3)
C(2)–N(3)	1·35 (2)	C(6)–C(7)	1·45 (3)
N(3)–C(4)	1·41 (2)	C(7)–C(8)	1·33 (3)
C(4)–C(9)	1·36 (3)	C(8)–C(9)	1·43 (3)
C(4)–C(5)	1·39 (3)	C(9)–N(1)	1·39 (2)
pmdt ligands			
N(11)–C(12)	1·40 (3)	N(21)–C(22)	1·49 (2)
N(11)–C(13)	1·44 (3)	N(21)–C(23)	1·45 (3)
N(11)–C(14)	1·57 (3)	N(21)–C(24)	1·50 (3)
C(14)–C(15)	1·31 (3)	C(24)–C(25)	1·54 (3)
C(15)–N(16)	1·41 (3)	N(26)–C(25)	1·47 (2)
N(16)–C(17)	1·48 (4)	N(26)–C(27)	1·49 (3)
N(16)–C(18)	1·45 (3)	N(26)–C(28)	1·464 (19)
C(18)–C(19)	1·38 (4)	C(28)–C(29)	1·51 (2)
N(110)–C(19)	1·53 (4)	N(210)–C(29)	1·47 (3)
N(110)–C(111)	1·40 (3)	N(210)–C(211)	1·49 (2)
N(110)–C(112)	1·48 (4)	N(210)–C(212)	1·49 (2)

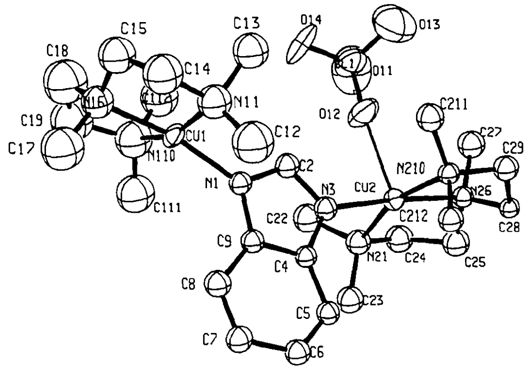

Fig. 8. *ORTEP* (Johnson, 1965) diagram of the [Cu(pmdt)]$_2$(Bzim)(ClO$_4$)$^{2+}$ cation showing the labeling scheme. Only the Cu, Cl and O atoms were given anisotropic temperature factors. See the caption to Fig. 2.

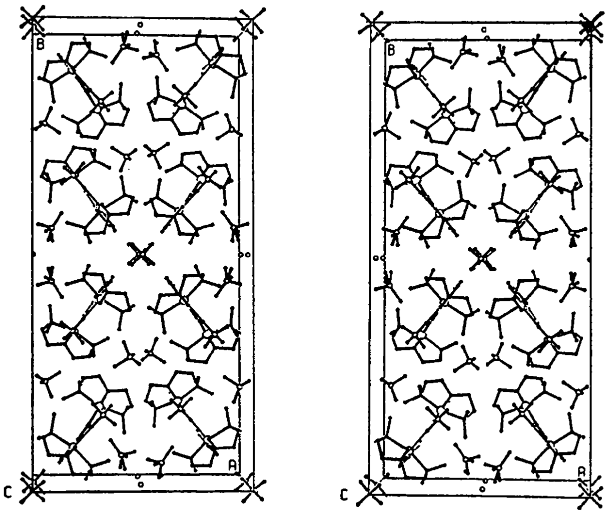

Fig. 9. Stereo *ORTEP* drawing showing the unit-cell contents of (6). Atoms are shown as spheres of arbitrary size.

It is interesting that the Cu(1)—N bond lengths are systematically 0·05 (1) Å shorter than the Cu(2)—N bond lengths. This difference may reflect the absence of an axial-site ligand to Cu(1). A dihedral angle of 146·1° is made by the two copper coordination planes. The Bzim dimensions are normal within statistical limits, which are large in this structure determination. Atoms C(5), C(6), C(7) and C(8) apparently are misplaced due no doubt to some error introduced by the quality of the crystal; the result is a rather irregular geometry for the fused benzene ring. The geometry of the im ring is satisfactory, however, and the entire Bzim group is planar to within 0·02 Å.

The crystal structure (Fig. 9) is composed of columns of cations extending along [001]. Channels parallel to the *c* axis are formed by the packing of the cations and these channels are occupied by uncoordinated perchlorate groups. The channel at $(\frac{1}{2}, 0, z)$ as well as the three symmetry-related channels are occupied by ClO_4(IV) and atom O(W). Those channels at $(\frac{1}{2}, 0{\cdot}28, z)$ and $(\frac{1}{2}, \frac{1}{2}, z)$ are filled with ClO_4(III) and ClO_4(II) respectively. There are no unusually close intermolecular contacts.

A comparison with other imidazole and im-bridged structures may be found in Kolks (1980).

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