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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.061
wR factor = 0.164
Data-to-parameter ratio = 10.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tetra- μ -1,1'-dimethyl-2,2'-bi-1*H*-imidazole-bis[aquacopper(II)] tetranitrate hexahydrate

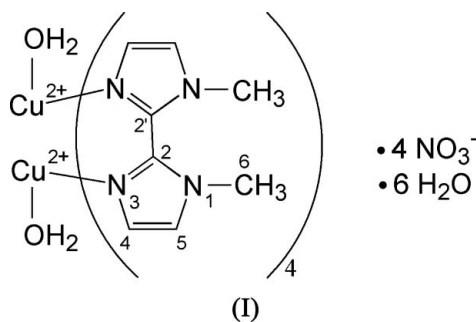
The crystal structure of the title compound, $[\text{Cu}_2(\text{C}_8\text{H}_{10}\text{N}_4)_4(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, contains dinuclear complex cations with twofold rotation symmetry, in which two Cu^{II} centers are bridged by four 1,1'-dimethyl-2,2'-bi-1*H*-imidazole ligands. Four N donors define the base of a slightly distorted square pyramid around each Cu^{II} center, the apical position being occupied by an aqua ligand. The nitrate ions and uncoordinated water molecules form a network of hydrogen bonds, in which the aqua ligands are also involved. The large $\text{Cu} \cdots \text{Cu}$ separation [3.092 (1) Å] is consistent with the absence of substantial metal–metal interactions, as suggested by the normal magnetic moment observed at room temperature.

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Comment

In a previous study of oxo–Re compounds (Fortin & Beauchamp, 2000), we noticed that unusual dinuclear frameworks can be developed with the *N,N'*-dimethyl-2,2'-biimidazole ligand (Me_2biim). In contrast with unsubstituted biimidazole, steric hindrance between the methyl groups in the *syn* conformation twists the two rings out of the plane and induces a preference for this molecule to act as a bridging rather than a chelating ligand. Various unusual di- and trinuclear Cd^{II} and Zn^{II} species were recently described by Sang & Xu (2005). The ability of this ligand to generate dinuclear units is exemplified here by the formation of the unprecedented $[\text{Cu}_2(\text{Me}_2\text{biim})_4(\text{H}_2\text{O})_2]^{4+}$ complex cation.



In the complex of the title compound, (I), four Me_2biim ligands 90° apart create a cage around the $\text{Cu} \cdots \text{Cu}$ axis (Fig. 1). Each of these ligands provides one N donor to each Cu center, generating the base of an approximate square pyramid, whose apical site is occupied by an aqua ligand. The Cu atom is displaced 0.883 (2) Å above the basal N_4 mean plane. The Cu–N distances [1.994 (3)–2.029 (3) Å] are similar to those found in $[\text{Cu}(\text{1-methylimidazole})_4]^{2+}$ and related complexes (Clegg *et al.*, 1988, and references therein). The Cu–O distance of 2.199 (3) Å is relatively short for an apical

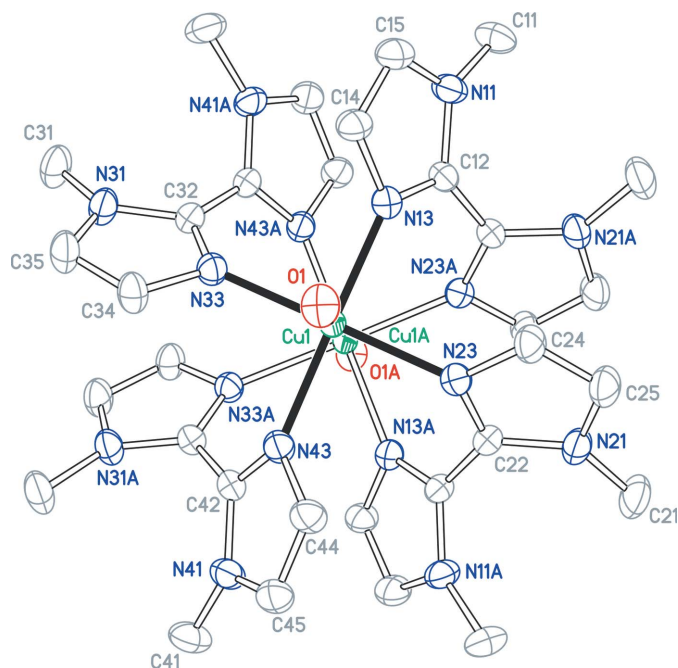


Figure 1
A view of the $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{Me}_2\text{biim})_4]^{4+}$ cation. The complex possesses a crystallographic twofold axis perpendicular to the $\text{Cu}\cdots\text{Cu}$ direction and horizontal in the plane of the figure. In the numbering scheme, the first digit corresponds to ring number and the second digit to the position in the ring. The suffix *A* corresponds to symmetry code (i) in Table 1. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted.

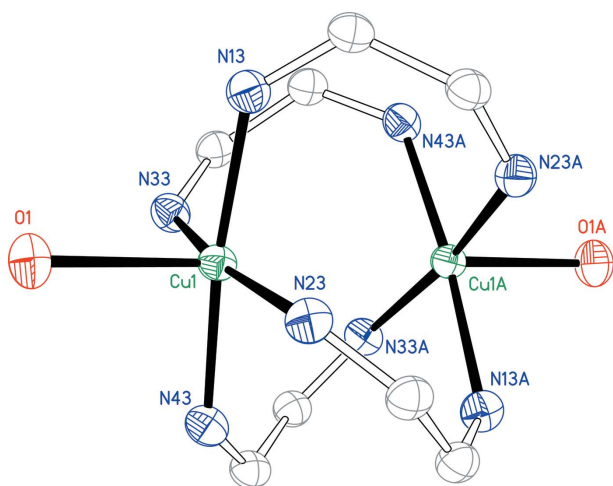


Figure 2
A simplified view of the $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{Me}_2\text{biim})_4]^{4+}$ cation, down the crystallographic twofold axis.

$\text{Cu}-\text{OH}_2$ bond, the typical distance for a five-coordinate species being 2.33 Å (Orpen *et al.*, 1995). No major changes are noted in the ligand bond lengths and angles with respect to free Me_2biim (Therrien & Beauchamp, 1999).

The inter-ring angles observed here [$\text{N}3-\text{C}2-\text{C}2'-\text{N}3' = 52.6(5)-53.1(5)^\circ$] are similar to those found in the infinite $[\text{Ag}(\text{Me}_2\text{biim})_n]^{n+}$ helicoidal chain (Gruia *et al.*, 2005) and slightly smaller than in the Re compound (65° ; Fortin & Beauchamp, 2000). As a consequence of non-coplanarity, the

two CuN_4 units in the dinuclear species are rotated 45° with respect to one another about the $\text{Cu}\cdots\text{Cu}$ direction. This staggered orientation allows the metal to lie relatively close to the expected lone pair direction of the N donors. The $\text{Cu}-\text{N}3-\text{C}2$ angles [$130.9(3)-131.4(3)^\circ$] are systematically greater than $\text{Cu}-\text{N}3-\text{C}4$ [$120.7(3)-121.8(3)^\circ$], but this difference is common for biimidazole complexes (Fortin & Beauchamp, 2001*a,b*, and references therein). Ideally, for each imidazole unit, the Cu atom should be coplanar with the ring. The Cu-to-plane distances observed are significant [0.133(6)–0.357(6) Å] but not exceedingly large. On the other hand, the external angles at C2 [$\text{N}1-\text{C}2-\text{C}2' = 123.3(3)-125.6(3)^\circ$] and $\text{N}3-\text{C}2-\text{C}2' = 124.7(3)-126.8(3)^\circ$] are virtually equal, so that the strain present in this region when biimidazole forms a chelate is relieved in the present bridged system. Thus, the N donor atoms fulfill standard requirements for efficient coordination. The imidazole rings make dihedral angles of $48.0(1)-51.0(1)^\circ$ with the basal N_4 plane of the square pyramid. This angle is imposed here by the molecular framework, but it lies in the broad range ($51-86^\circ$) found for this angle in 1-methylimidazole complexes (Clegg *et al.*, 1988).

Fig. 1 reveals that the $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{Me}_2\text{biim})_4]^{4+}$ complex cation has an approximate fourfold axis along the $\text{Cu}\cdots\text{Cu}$ axis. Perpendicular to this direction are found four approximate twofold axes 45° apart, one of which (Fig. 2) is a crystallographic symmetry element. Therefore, the idealized symmetry is $422 (D_4)$.

The crystal structure contains layers of thickness $b/2$ parallel to the ac plane, in which the cations are connected by a hydrogen-bonding network involving the apical aqua ligand, nitrate ions and uncoordinated water molecules. Details of hydrogen bonds are provided in Table 2.

The large $\text{Cu}\cdots\text{Cu}$ distance of 3.092(1) Å in the dinuclear species suggests that the two Cu centers can be regarded as magnetically independent. This assumption is supported by the room-temperature magnetic moment, which corresponds to a normal value of 1.83 BM per Cu^{II} center. The non-planar arrangement of the ligand rings, which breaks the connection between the aromatic systems, is another factor that probably prevents the interaction between the Cu centers.

Experimental

Me_2biim was prepared according to the method described by Mohanty *et al.* (1994), by methylation of 2,2-biimidazole, obtained by the method of Fiesemann *et al.* (1978). The complex was obtained by reacting the ligand and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in a 2:1 ratio. The copper salt (23.2 mg, 0.10 mmol) was dissolved in methanol (2 ml) and Me_2biim (32.4 mg, 0.20 mmol) was added to the stirred mixture. A dark-blue powder formed quickly, which was filtered off, washed with diethyl ether and dried in a desiccator over Drierite. Analysis, calculated for $\text{C}_{32}\text{H}_{44}\text{N}_{20}\text{O}_{14}\text{Cu}_2$: C 36.26, N 26.43, H 4.18%; found: C 36.41, N 26.38, H 4.20%. IR frequencies (cm^{-1}): 3429 (*br*), 3121 (*m*), 3021 (*sh*), 2925 (*w*), 1742 (*w*), 1635 (*br*), 1532 (*m*), 1499 (*s*), 1463 (*s*), 1384 (*vs*), 1320 (*sh*), 1281 (*s*), 1215 (*m*), 1169 (*m*), 1151 (*s*), 1039 (*w*), 962 (*m*), 948 (*sh*), 828 (*sh*), 794 (*s*), 739 (*s*), 727 (*s*), 685 (*m*), 628 (*w*), 507 (*w*), 465 (*w*), 405 (*w*), 350 (*w*), 320 (*w*), 285 (*w*). Magnetic moment $\mu_{\text{eff}} = 1.83$ BM (based on the monomeric formula). Crystals

of the hexahydrate suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a moist methanol solution.

Crystal data

[Cu₂(C₈H₁₀N₄)₄(H₂O)₂](NO₃)₄·6H₂O
M_r = 1168.05
 Monoclinic, *C*2/*c*
a = 21.3104 (2) Å
b = 22.0240 (2) Å
c = 11.0725 (1) Å
 β = 108.865 (1)°
V = 4917.61 (8) Å³
Z = 4

D_x = 1.578 Mg m⁻³
 Cu Kα radiation
 Cell parameters from 25 reflections
 θ = 20.0–23.0°
 μ = 1.90 mm⁻¹
T = 293 (2) K
 Block, blue
 0.35 × 0.26 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/2θ scans
 Absorption correction: Gaussian (ABSORP in NRCVAX; Gabe *et al.*, 1989)
T_{min} = 0.560, *T_{max}* = 0.649
 33942 measured reflections
 4727 independent reflections

3670 reflections with *I* > 2σ(*I*)
R_{int} = 0.190
 θ_{max} = 70.6°
h = -26 → 26
k = -26 → 26
l = -13 → 13
 4 standard reflections
 frequency: 60 min
 intensity decay: 0.2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.061
wR(*F*²) = 0.164
S = 0.95
 4727 reflections
 434 parameters

H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(*F_o*²) + (0.124*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.003
 Δρ_{max} = 0.99 e Å⁻³
 Δρ_{min} = -0.98 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–N13	1.994 (3)	Cu1–N43	1.997 (3)
Cu1–N23	2.016 (3)	Cu1–O1	2.199 (3)
Cu1–N33	2.029 (3)		
N13–Cu1–N43	173.04 (13)	C14–N13–Cu1	121.3 (3)
N23–Cu1–N33	168.22 (13)	N23–C22–C12 ⁱ	126.8 (3)
N13–Cu1–N23	90.22 (13)	N21–C22–C12 ⁱ	123.3 (3)
N13–Cu1–N33	88.66 (13)	C22–N23–Cu1	130.9 (3)
N43–Cu1–N23	88.88 (12)	C24–N23–Cu1	121.8 (3)
N43–Cu1–N33	90.81 (12)	N33–C32–C42 ⁱ	126.5 (3)
N13–Cu1–O1	93.13 (13)	N31–C32–C42 ⁱ	123.7 (3)
N43–Cu1–O1	93.83 (13)	C32–N33–Cu1	131.4 (3)
N23–Cu1–O1	96.34 (12)	C34–N33–Cu1	121.6 (3)
N33–Cu1–O1	95.43 (12)	N43–C42–C32 ⁱ	124.7 (3)
N13–C12–C22 ⁱ	125.3 (3)	N41–C42–C32 ⁱ	125.6 (3)
N11–C12–C22 ⁱ	125.1 (3)	C42–N43–Cu1	131.4 (3)
C12–N13–Cu1	131.1 (3)	C44–N43–Cu1	120.7 (3)

Symmetry code: (i) -*x*, *y*, -*z* + 3/2.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H1A...O3 ⁱⁱ	0.82 (4)	1.94 (4)	2.760 (5)	175 (5)
O1–H1B...O2 ⁱⁱⁱ	0.82 (3)	1.94 (3)	2.757 (5)	173 (5)
O2–H2A...O4	0.87 (6)	1.90 (6)	2.717 (6)	155 (7)
O2–H2B...O31	0.82 (4)	2.02 (4)	2.722 (9)	143 (6)
O2–H2B...O33 ^{iv}	0.82 (4)	2.03 (5)	2.833 (15)	166 (6)
O3–H3A...O23 ^v	0.82 (4)	2.04 (5)	2.86 (3)	180 (5)
O3–H3A...O21	0.82 (4)	2.08 (6)	2.89 (5)	173 (3)
O3–H3B...O11	0.85 (3)	2.09 (2)	2.883 (12)	153 (7)

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O4–H4A...O23 ^v	0.82 (5)	2.02 (3)	2.83 (3)	171 (9)
O4–H4A...O21 ^v	0.82 (5)	2.15 (7)	2.96 (4)	167 (9)
O4–H4B...O23 ⁱⁱ	0.82 (7)	2.01 (3)	2.81 (3)	168 (9)

Symmetry codes: (ii) *x*, *y*, *z* + 1; (iii) -*x* + 1/2, -*y* + 1/2, -*z* + 2; (iv) -*x* + 1, *y*, -*z* + 3/2; (v) *x*, -*y*, *z* + 1/2.

All nitrate ions were found to be involved in twofold disorder. Restraints were applied in the refinement to keep their geometry close to trigonal planar. Nitrates N1 and N3 lie close to crystallographic twofold axes, where they were disordered over two orientations with occupancies of 0.50 fixed by symmetry. The N2/N2' anion was described as two components in general positions. Occupancies were initially refined for a few cycles and then fixed to the normalized values (0.43/0.57) for the rest of the refinement. The C-bonded H atoms were positioned geometrically (C–H = 0.93 Å for ring atoms and 0.96 Å for methyl H atoms) and were included in the refinement in the riding-model approximation. The H atoms of the water molecules were positioned from residual peaks in the difference Fourier map. The water H atoms were refined, but restraints were imposed to keep the O–H bond length and the H–H separation close to 0.82 (4) and 1.29 (5) Å, respectively. The *U*_{iso}(H) values were set to 1.5 times (1.2 for ring C–H) *U*_{eq}(parent). A final check for possible voids was performed with PLATON (Spek, 2003).

Data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: NRC-2 (Ahmed *et al.*, 1973); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: UDMX (Maris, 2004).

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