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Key indicators

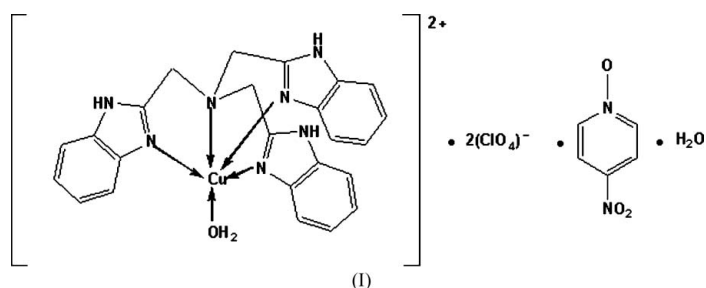
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.045
 wR factor = 0.131
Data-to-parameter ratio = 14.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aqua[tris(1*H*-benzimidazol-2-ylmethyl)-
amine]copper(II) bis(perchlorate)
4-nitropyridine *N*-oxide monohydrate

In the title structure, $[\text{Cu}(\text{C}_{24}\text{H}_{21}\text{N}_7)(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{C}_5\text{H}_4\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the Cu^{II} atom is bonded to a tris(1*H*-benzimidazol-2-ylmethyl)amine (ntb) ligand and a water molecule through four N atoms and one O atom, giving a distorted trigonal-bipyramidal coordination geometry with approximate C_3 molecular symmetry.

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Comment

The asymmetric unit of the title compound, (I) (Fig. 1), consists of one $[\text{Cu}(\text{ntb})(\text{H}_2\text{O})]^{2+}$ cation [ntb is tris(1*H*-benzimidazol-2-ylmethyl)amine], two perchlorate anions, one molecule of 4-nitropyridine *N*-oxide and one molecule of water of crystallization, which is disordered over two sites with equal occupancies. The Cu^{II} atom is five-coordinate with an N_4O ligand set. The ntb ligand acts as a tetradentate *N*-donor and an aqua O atom completes the coordination. The coordination geometry of the Cu^{II} atom is best described as distorted trigonal-bipyramidal, with approximate molecular site symmetry C_3 . The coordination geometry around the Cu^{II} atoms appears to relieve steric crowding. The equatorial plane is occupied by three N atoms of three benzimidazolyl groups, while the Cu^{II} atom protrudes towards O1 and is 0.319 (1) Å from the plane of atoms N3/N5/N7. The axial positions are occupied by N1 and O1. Selected bond lengths and angles are listed in Table 1.



The three benzimidazole ring arms of the ntb ligand form a cone-shaped cavity. The distortions of the $\text{N1}-\text{Cu1}-\text{N3}$, $\text{N1}-\text{Cu1}-\text{N5}$ and $\text{N1}-\text{Cu1}-\text{N7}$ angles, which are all *ca* 10° less than the ideal 90° , are imposed by the geometry of the ntb ligand. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, along with weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and a single significant $\pi-\pi$ stacking interaction [where $\text{Cg1}\cdots\text{Cg1}(2-x, -y, 1-z) = 3.6833(3)\text{ \AA}$ (Cg1 is the centroid of ring atoms $\text{C10}/\text{N4}/\text{C11}/\text{C16}/\text{N5}$) and the perpendicular distance is 3.49 \AA] connect cations, anions and solvent molecules into a three-dimensional network (Table 2 and Fig. 2)

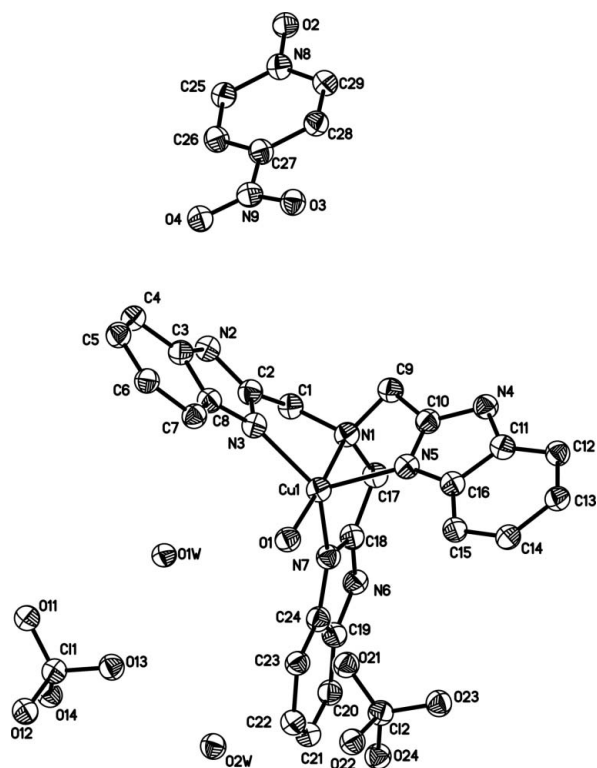


Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted. Both disorder components are shown.

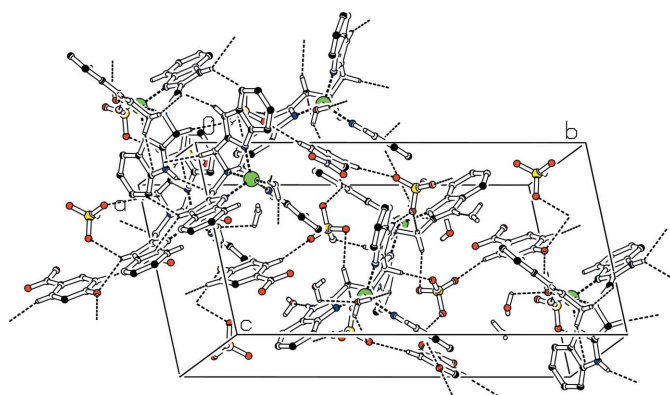


Figure 2
Partial packing plot (Spek, 2003) of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Experimental

To a stirred solution of tris(1*H*-benzimidazol-2-ylmethyl)amine (407 mg, 1 mmol) in methanol (20 ml), Cu(ClO₄)₂·6H₂O (370 mg, 1 mmol) was added, followed by the addition of a solution of 4-nitropyridine *N*-oxide (140 mg, 1 mmol) in methanol (5 ml). The resulting clear blue solution was stirred for 8 h and then allowed to stand at room temperature. Blue–green crystals suitable for X-ray diffraction studies were obtained after three weeks (yield 437 mg,

51%). Analysis, found: C 40.95, H 3.41, N 14.63%; calculated for C₂₉H₂₉Cl₂CuN₉O₁₃: C 41.17, H 3.43, N 14.89%.

Crystal data

[Cu(C₂₄H₂₁N₇)(H₂O)](ClO₄)₂·
C₅H₄N₂O₃·H₂O
M_r = 846.05
Monoclinic, *P*2₁/*n*
a = 11.986 (3) Å
b = 24.134 (6) Å
c = 14.226 (3) Å
β = 114.913 (1)°

V = 3732.2 (15) Å³
Z = 4
D_x = 1.506 Mg m⁻³
Mo Kα radiation
μ = 0.80 mm⁻¹
T = 298 (2) K
Block, blue–green
0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-
detector diffractometer
φ and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2000)
*T*_{min} = 0.83, *T*_{max} = 0.85

19956 measured reflections
7345 independent reflections
5401 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.012
θ_{max} = 26.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.045
wR (*F*²) = 0.131
S = 1.00
7345 reflections
496 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.07*P*)²
+ 1.99*P*]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.35 e Å⁻³
Δρ_{min} = -0.34 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	1.957 (2)	Cu1–N5	2.085 (3)
Cu1–N3	1.992 (3)	Cu1–N1	2.127 (3)
Cu1–N7	2.023 (3)		
O1–Cu1–N3	96.50 (10)	N7–Cu1–N5	106.90 (11)
O1–Cu1–N7	98.53 (10)	O1–Cu1–N1	176.53 (10)
N3–Cu1–N7	128.01 (11)	N3–Cu1–N1	80.78 (11)
O1–Cu1–N5	102.72 (10)	N7–Cu1–N1	81.59 (11)
N3–Cu1–N5	117.68 (11)	N5–Cu1–N1	80.52 (11)

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–H1C···O21	0.85	2.44	3.230 (4)	156
O1–H1E···O2 ⁱ	0.82	2.17	2.807 (3)	135
O1W–H1WC···O1	0.85	2.34	2.733 (5)	108
N4–H4A···O2 ⁱⁱ	0.86	2.57	3.274 (4)	139
N4–H4A···O14 ⁱⁱ	0.86	2.48	3.159 (4)	136
N6–H6A···O24 ⁱⁱⁱ	0.86	2.14	2.964 (4)	161
C1–H1A···O12 ^{iv}	0.97	2.49	3.353 (5)	147
C1–H1B···O24 ^v	0.97	2.54	3.469 (5)	160
C17–H17B···O11 ⁱⁱ	0.97	2.38	3.265 (4)	152
C26–H26···O4	0.93	2.38	2.704 (5)	100
C26–H26···O13 ^{vi}	0.93	2.47	3.284 (4)	146
C29–H29···O23 ^{vii}	0.93	2.55	3.183 (4)	126

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y, -z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x + 1, y, z$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

H atoms bonded to atom O1 were located in a difference Fourier map and were refined in a riding-model approximation, with *U*_{iso}(H)

= $1.2U_{\text{eq}}(\text{O})$, or $1.5U_{\text{eq}}(\text{O})$ for H1E. All other atoms were placed in calculated positions, with C–H = 0.93–0.97 Å, N–H = 0.86 Å and O–H = 0.85 Å, and refined in a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

- Bruker (2000). *SMART, SAINT, SADABS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
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