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{2-(4,7-Dimethyl-1,4,7-triazacyclonon-1-yl)-*N*-methyl-*N*-[(1-methylbenzimidazol-2-yl)methyl]ethylamine}-copper(II) bis(perchlorate)

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In the title compound, $[Cu(C_{20}H_{34}N_6)](ClO_4)_2$, the Cu^{II} atom is coordinated to the five ligand donor N atoms of the pendant-arm macrocyclic ligand. The coordination sphere geometry can be described as either distorted square-pyramidal or distorted trigonal-prismatic.

Key indicators

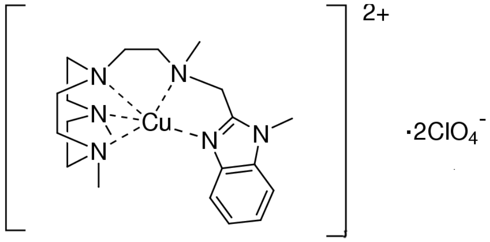
Single-crystal X-ray study
T = 213 K
Mean σ(C–C) = 0.006 Å
R factor = 0.054
wR factor = 0.165
Data-to-parameter ratio = 9.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Galactose oxidase is a non-blue copper-dependent oxidase isolated from *Dactylium dendroides* (Ogel *et al.*, 1994) and structurally characterized (Ito *et al.*, 1992). This enzyme achieves the stereoselective oxidation of primary alcohols, such as D-galactose. There has been some interest in the potential utility of this enzyme as a biosensor (Hasebe & Uchiyama, 2000). Extensive spectroscopic investigations have probed the mechanism of catalysis indicating a pH dependence of the redox reaction, providing evidence for a phenolic amino acid residue initiating the catalytic cycle by abstraction of an H atom from a neighbouring group (Reynolds *et al.*, 1997).

Recently, this enzyme has attracted our interest and we have prepared structural model complexes (Daly & Martin, 2001) containing the square-based pyramidal geometry about the Cu^{II} ion, as observed in the native enzyme. Unfortunately, we were unable to structurally characterize the ligand containing the phenol moiety in the solid state; however, the title complex, (I), is the *N*-methyl derivative coordinated to a Cu^{II} ion.



(I)

If the coordination of Cu^{II} is described as distorted square-pyramidal the N1, N3, N4 and N5 atoms would constitute the base plane and N2, which has the longest bond to Cu^{II} (Table 1), is the apical atom. Deviations from the least-squares plane through N1, N3, N4 and N5 are 0.191 (4), −0.262 (5), −0.226 (4) and 0.200 (4) Å, respectively, so that there is a significant tetrahedral distortion from planarity. Cu and N2

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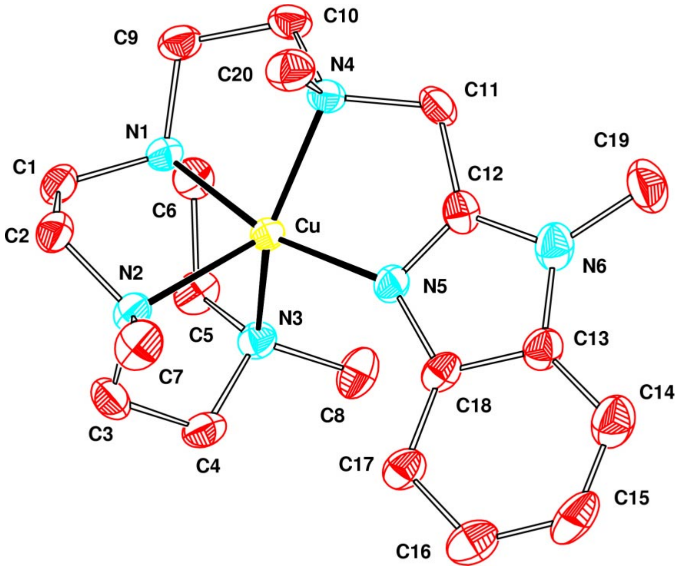

Figure 1
The complex cation of the title compound with displacement ellipsoids at the 50% probability level.

are 0.381 (1) and 2.350 (4) Å from this plane. This pentadentate ligand coordinates in a different conformation in the octahedral Ni complex (Daly *et al.*, 2001) which has acetonitrile as the sixth ligand. There, N2, N3, N4 and N5 are in a square plane, with N1 at the apex.

An alternative trigonal-bipyramidal description arises from considering N2, N3 and N4 as the triangular entity. In this description, N1, N5 and Cu are 1.842 (3), −2.101 (4) and −0.180 (1) Å, respectively, from this equatorial plane.

Experimental

To a refluxing solution of the ligand (0.639 g, 1.78 mmol) in a 1:1 water/ethanol (10 ml) mixture was added dropwise an aqueous solution of copper perchlorate hexahydrate (0.661 g, 1.78 mmol, 5 ml). The mixture, now a deep blue colour, was heated for a further 5 min then acetonitrile (∼1 ml) was added and the solution allowed to cool. The dark-blue crystals that formed, after further cooling (in a refrigerator) were collected by filtration, washed with a small amount of water then ethanol prior to being air dried. Yield = 0.50 g (45%). λ_{max}CH$_3$CN, 648 nm, ε = 311.51 M^{-1} cm^{-1}, μ = 2.13 μ_B at 291 K. Microanalysis for $C_{20}H_{34}Cl_2CuN_6O_8$, calculated: C 38.68, H 5.52, N 13.53%; found: C 38.55, H 5.34, N 13.42%. Suitable crystals of the complex were grown by slow evaporation of a solution of the complex in ∼5% acetonitrile/water mixture.

Crystal data

$[Cu(C_{20}H_{34}N_6)](ClO_4)_2$
M_r = 620.98
Orthorhombic, *Pbca*
a = 12.978 (2) Å
b = 16.518 (2) Å
c = 23.950 (4) Å
V = 5134 (1) Å^3
Z = 8
D_x = 1.607 Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 48.6–49.8°
μ = 3.64 mm^{-1}
T = 213.2 K
Irregular, blue
0.40 × 0.28 × 0.20 mm

Data collection

Rigaku AFC-6*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.382, T_{max} = 0.483
3823 independent reflections
3263 reflections with $F^2 > 1.5\sigma(F^2)$

θ_{max} = 60.1°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 26$
3 standard reflections every 150 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 1.5\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.165
S = 1.38
3263 reflections
334 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1F_o^2)^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.022 (3)	Cu—N4	2.053 (3)
Cu—N2	2.194 (3)	Cu—N5	2.000 (3)
Cu—N3	2.091 (3)		
N1—Cu—N2	83.33 (12)	N2—Cu—N4	129.11 (12)
N1—Cu—N3	85.23 (13)	N2—Cu—N5	110.22 (12)
N1—Cu—N4	85.97 (13)	N3—Cu—N4	144.42 (13)
N1—Cu—N5	165.60 (13)	N3—Cu—N5	100.68 (13)
N2—Cu—N3	83.84 (12)	N4—Cu—N5	81.62 (13)

There is a peak of 1.195 e Å^{-3} 0.94 Å from Cl1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997); program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structure: *Xtal*3.4 *CRYLSQ* (Hall *et al.*, 1995); molecular graphics: *Xtal*3.4 *PIG ORTEP*; software used to prepare material for publication: *Xtal*3.4 *BONDLA CIFIO*.

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