

Di- μ -hydroxido-bis[[bis(6-methyl-2-pyridylmethyl)(2-phenylethyl)amine- $\kappa^3 N', N'', N'''$]]copper(II) bis(perchlorate)

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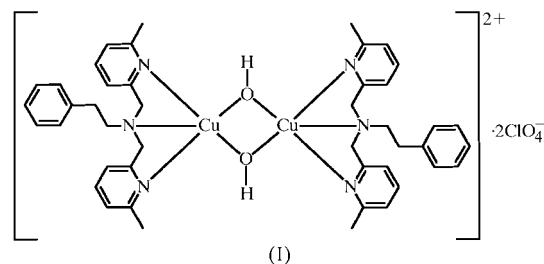
The title compound, $[\text{Cu}_2(\text{OH})_2(\text{C}_{22}\text{H}_{25}\text{N}_3)_2](\text{ClO}_4)_2$, is a copper(II) dimer, with two $[\text{CuL}]^{2+}$ units [L is bis(6-methyl-2-pyridylmethyl)(2-phenylethyl)amine] bridged by hydroxide groups to define the $\{[\text{CuL}](\mu\text{-OH})_2[\text{CuL}]\}^{2+}$ cation. Charge balance is provided by perchlorate counter-anions. The cation has a crystallographic inversion centre halfway between the Cu^{II} ions, which are separated by 3.0161 (8) Å. The central core of the cation is an almost regular Cu_2O_2 parallelogram of sides 1.931 (2) and 1.935 (2) Å, with a $\text{Cu}-\text{O}-\text{Cu}$ angle of 102.55 (11)°. The coordination geometry around each Cu^{II} centre can be best described as a square-based pyramid, with three N atoms from L ligands and two hydroxide O atoms completing the coordination environment. Each cationic unit is hydrogen bonded to two perchlorate anions by means of hydroxide-perchlorate $\text{O}-\text{H}\cdots\text{O}$ interactions.

Comment

The discovery that the reaction of molecular oxygen with aromatic organic substrates can be catalyzed by Cu^{I} complexes has led to increasing interest in the study of its properties (Spodine & Manzur, 1992; Mizuno *et al.*, 2006). It has also attracted interest for modelling oxygen-carrying (van Holde *et al.*, 2001) and oxygenating or oxidoreductase proteins (Solomon *et al.*, 2001; Brazeau *et al.*, 2004). Normally, dihydroxide-bridged dicopper(II) complexes are the final products of the reaction between cuprous complexes and dioxygen (Mirica *et al.*, 2004; Rojas *et al.*, 2004). In this context, one of the most interesting families of ligands is the bis-(pyridine-2-ylalkyl)amines (Mirica *et al.*, 2004; Shearer *et al.*, 2005), since their steric and electronic properties can be varied over a wide range (Hayashi *et al.*, 2000).

The structure of the title compound, (I), consists of a molecular cation with the charge counterbalanced by two

perchlorate anions. The molecular dication corresponds to a dimer exhibiting two $[\text{CuL}]^{2+}$ units [L is bis(6-methyl-2-pyridylmethyl)(2-phenylethyl)amine] which are connected by



two hydroxide ligands, acting in a μ_2 -fashion. The ligand L is connected to each Cu^{II} centre in a tridentate fashion through its N donor atoms. The coordination geometry around each Cu^{II} centre is best described as a square-based pyramid ($\tau < 0.01$; Addison *et al.*, 1984), with two pyridyl N atoms (N1 and N3) and two hydroxide O atoms [O1 and O1ⁱ; symmetry code: (i) $1 - x, 1 - y, 1 - z$] in a *cis* configuration occupying the basal positions, leaving amine atom N2 in the remaining apical position. The dication is then constructed around a central Cu_2O_2 parallelogram of sides 1.931 (2) (Cu1—O1) and 1.935 (2) Å (Cu1—O1ⁱ), with a $\text{Cu}-\text{O}-\text{Cu}$ angle of 102.55 (11)°. The existence of a crystallographic inversion centre is a consequence of the *anti* configuration of both apical sites with respect to the central Cu_2O_2 plane. This coordination mode for tridentate 6-methylpyridylamine complexes has

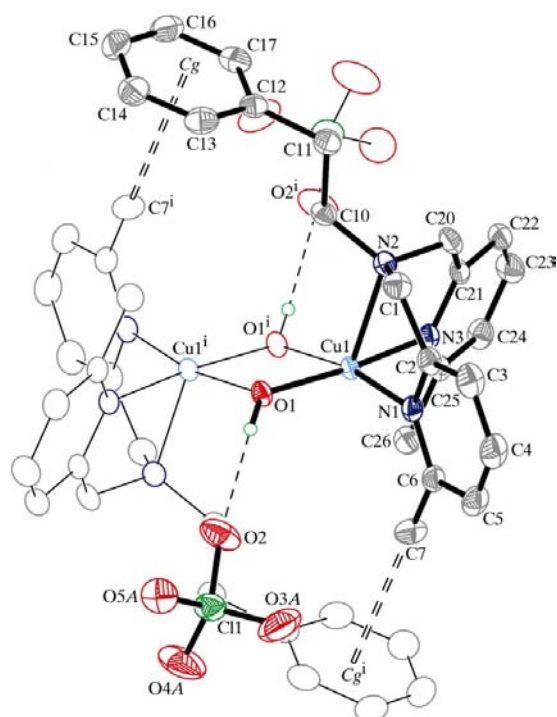


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. The H atoms of the organic ligand and the minor component of the disordered counter-ion have been omitted for clarity. Hydrogen bonds are shown as single dashed lines and π - π contacts as double-dashed lines. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

been described previously in related cupric compounds as an amine-*ele* mode (Rojas *et al.*, 2004; Manzur *et al.*, 2007). The measured Cu^{II}··Cu distance is 3.0161 (8) Å, which lies in the longest segment of the values described for this coordination mode in some closely related complexes (Rojas *et al.*, 2004; Manzur *et al.*, 2007).

Interestingly, the centroid of the C12–C17 phenyl group on the 2-phenylethyl arm of the *L* ligand coordinated to one of the Cu^{II} centres points directly to the methyl group [C7ⁱⁱ; symmetry code: (ii) 2 - x, 2 - y, 1 - z] of the neighbouring *L* ligand in the dimer. The centroid-to-carbon distance, Cg1··C7ⁱⁱ, is 3.671 (1) Å, while the three H··Cg1 distances amount to 3.47 (1) Å.

As described for [L'(CH₃CN)Cu(μ-OH)₂Cu(CH₃CN)L']-(ClO₄)₂, where *L'* is bis[dibenzyl(6-methyl-2-pyridylmethyl)-amine] (Rojas *et al.*, 2005), the perchlorate anions and hydroxide groups of (I) interact *via* hydrogen bonding (Fig. 1 and Table 2). These interactions result in the deviation of the O–H vector by 63.9° from the Cu₂O₂ plane, with each of the two H atoms on opposite sides of the plane. It has been pointed out that the deviation of these H atoms from the Cu₂O₂ plane plays an important role in determining the magnetic coupling exchange in binuclear copper(II) complexes (Ruiz *et al.*, 1997).

Although a packing view of the structure of (I) suggests some additional Cl–O··H interactions, the disorder observed for three of the perchlorate O atoms precludes their accurate characterization.

Experimental

The ligand bis(6-methyl-2-pyridylmethyl)(2-phenylethyl)amine was synthesized by the reaction of two equivalents of 2-bromomethyl-6-methylpyridine with 2-phenylethylamine (4.8 g, 0.04 mmol) in refluxing acetonitrile (150 ml) for 24 h in the presence of sodium carbonate (10 g). The title copper(II) dimer was obtained by the treatment of a dichloromethane solution of the copper(I) complex [prepared *in situ* from Cu(CH₃CN)₄ClO₄ and the ligand] with molecular oxygen at room temperature. After standing overnight, crystals of (I) suitable for X-ray diffraction studies were separated.

Caution: perchlorate complexes are potentially explosive and should be handled very carefully. The small quantities used in our studies were not found to present a hazard.

Crystal data

[Cu ₂ (OH) ₂ (C ₂₂ H ₂₅ N ₃) ₂](ClO ₄) ₂	<i>V</i> = 2229.0 (4) Å ³
<i>M_r</i> = 1022.92	<i>Z</i> = 2
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.9239 (11) Å	<i>μ</i> = 1.14 mm ⁻¹
<i>b</i> = 16.5696 (19) Å	<i>T</i> = 298 (2) K
<i>c</i> = 13.9248 (16) Å	0.41 × 0.17 × 0.13 mm
<i>β</i> = 103.229 (2)°	

Data collection

Siemens SMART CCD area-detector diffractometer	13767 measured reflections
Absorption correction: part of the refinement model (<i>ΔF</i>) (<i>SADABS</i> in <i>SAINT-NT</i> ; Bruker, 1999)	3964 independent reflections
<i>T_{min}</i> = 0.652, <i>T_{max}</i> = 0.866	2909 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.052

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.051	6 restraints
<i>wR</i> (<i>F</i> ²) = 0.137	H-atom parameters constrained
<i>S</i> = 1.00	<i>Δρ_{max}</i> = 0.56 e Å ⁻³
3964 reflections	<i>Δρ_{min}</i> = -0.31 e Å ⁻³
319 parameters	

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	1.931 (2)	Cu1–N1	2.039 (3)
Cu1–O1 ⁱ	1.935 (2)	Cu1–N2	2.263 (3)
Cu1–N3	2.040 (3)	Cu1··Cu1 ⁱ	3.0161 (8)
O1–Cu1–O1 ⁱ	77.45 (11)	O1 ⁱ –Cu1–N2	107.74 (11)
O1–Cu1–N3	167.88 (11)	N3–Cu1–N2	80.51 (12)
O1 ⁱ –Cu1–N3	90.44 (11)	N1–Cu1–N2	79.92 (12)
O1 ⁱ –Cu1–N1	167.82 (11)	Cu1–O1–Cu1 ⁱ	102.55 (11)

Symmetry code: (i) -x + 1, -y + 1, -z + 1.

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–H1···O2	0.88	2.15	2.999 (4)	161

H atoms bound to C atoms were included in calculated positions, with C–H = 0.93–0.97 Å, and allowed to ride, with *U*_{iso}(H) = 1.2 or 1.5 times *U*_{eq}(C). The hydroxide atom H1 was located in a difference Fourier map and its isotropic displacement parameter was subsequently refined, but its coordinates were kept fixed. During the final stages of refinement, some disorder was observed for the perchlorate O atoms not involved in hydrogen bonding (O3, O4 and O5). This was modelled using two positions, *A* and *B*, for each O atom. The partial occupancies were first refined and then held constant at the convergence values of 0.55 and 0.45, respectively. The Cl–O distance for the disordered atoms was restrained to be 1.42 (1) Å.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1999); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3038). Services for accessing these data are described at the back of the journal.

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