

Di- μ -hydroxo-bis{(acetonitrile)di-benzyl(6-methyl-2-pyridylmethyl)-amine- κ^2N,N]copper(II)} bis(perchlorate)

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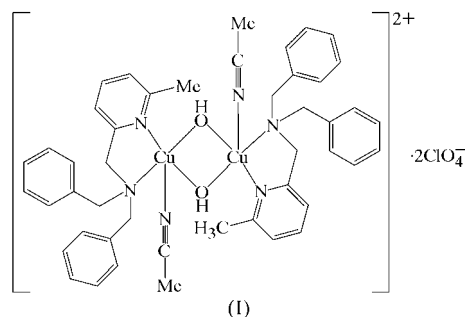
The title compound corresponds to a copper(II) dimer, $[\text{Cu}_2(\text{OH})_2(\text{C}_2\text{H}_3\text{N})_2(\text{C}_{21}\text{H}_{22}\text{N}_2)_2](\text{ClO}_4)_2$, where the metal centres are μ_2 -bridged by hydroxo groups. The coordination of each copper(II) centre is a slightly distorted square-based pyramid, with two N atoms from dibenzyl(6-methyl-2-pyridylmethyl)amine (BiBzMePMA) and two hydroxo O atoms occupying the basal positions, and the acetonitrile N atom at the apical position. The dimer is centrosymmetric, with a crystallographic inversion centre midway between the two Cu atoms [$\text{Cu} \cdots \text{Cu} = 2.9522(9) \text{ \AA}$]

Comment

The coordination chemistry of copper complexes is a subject of continuing importance, mainly in relation to the structure and reactivity of the active site in copper-containing metalloproteins. The reactivity of copper(I) complexes towards molecular oxygen is also relevant to the utilization of atmospheric oxygen in stoichiometric or catalytic oxidations of organic substrates mediated by copper complexes (Karlin *et al.*, 1999), as well as to understanding the mechanism of dioxygen utilization by copper proteins (Karlin & Zuberbuhler, 1999; Kopf & Karlin, 2000; Solomon *et al.*, 1996). Recent advances (Kitajima & Moro-oka, 1994; Suzuki *et al.*, 2000) have shown that the structure and reactivity of copper(I) complexes are significantly modified by slight perturbations in the supporting ligands.

Recently, we reported that the oxygenation of a methanol solution of the copper(I) complex with the bidentate ligand dibenzyl(6-methyl-2-pyridylmethyl)amine (BiBzMePMA) at room temperature leads to the di- μ -methoxo-dicopper(II) complex $[\text{Cu}(\text{BiBzMePMA})_2-\mu_2-(\text{OCH}_3)_2]$, which has been fully characterized, both magnetically and structurally (Rojas *et al.*, 2004). We report here the crystal structure of the

analogous di- μ -hydroxo compound, $[\text{Cu}(\text{BiBzMePMA})_2-\mu_2-(\text{OH})_2]$, (I), resulting from the same synthetic procedure, but with traces of water in the solvent.



The molecular structure of complex (I) is defined by two $[\text{CuL}]^{2+}$ units [where L is dibenzyl(6-methyl-2-pyridylmethyl)amine], which are μ_2 -bridged by two hydroxo groups, in such a way as to define a central $\text{N}_2\text{CuO}_2\text{CuN}_2$ core. Additionally, there is an acetonitrile ($\text{CH}_3\text{C}\equiv\text{N}$) molecule completing the pentacoordination of each Cu atom, thus defining a slightly distorted square-based pyramidal coordination for the metal centres. The basal square of the pyramid is defined by two amine N atoms (N1 and N2) and two hydroxo O atoms [O1 and O1ⁱ; symmetry code: (i) $1 - x, -y, 2 - z$], while acetonitrile atom N3 occupies the apical position and deviates by 3.7° from the perpendicular to the basal-plane position.

The $\text{Cu}-\text{N}_{\text{acetonitrile}}$ distance is $2.476(5) \text{ \AA}$, a rather long value for this kind of bond, which is usually in the range $2.00\text{--}2.50 \text{ \AA}$. A shorter value of about 2 \AA has been reported for $[\text{Cu}_2(\text{L}_2)(\text{CH}_3\text{CN})_2]^{4+}$, where L is N,N,N',N' -tetrakis(1-methylimidazol-2-ylmethyl)-2-hydroxy-1,3-diaminopropane (Gentshev *et al.*, 2000), while a distance of $2.322(6) \text{ \AA}$ has been reported for $[\text{Cu}_2(\mu\text{-oxalato})(\text{dipyridylamino})_2(\text{CH}_3\text{-CN})_2](\text{ClO}_4)_2$ (Du *et al.*, 2003). The linear acetonitrile mol-

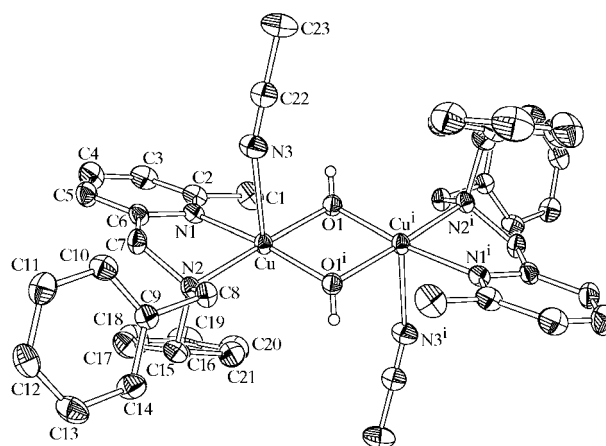


Figure 1
The molecular structure of (I), showing part of the atom-numbering scheme. Displacement ellipsoids are plotted at the 33% probability level and hydroxo H atoms are shown as small spheres of arbitrary radii. The remaining H atoms and the perchlorate counter-anion have been omitted for clarity. [Symmetry code: (i) $1 - x, -y, 2 - z$.]

ecule defines an angle of 24.8° with the Cu—N3 line [Cu—N3—C22 = 155.2 (4)°], which can probably be ascribed to packing effects (Murthy *et al.*, 2001).

The two edge-sharing pyramids have their apical acetonitrile N atoms lying on opposite sides of the CuO₂Cu plane, in a *trans* arrangement, as required by the inversion centre at the middle of the Cu···Cu distance. A *cis* arrangement was found in the macrocyclic complex [Cu₂L(CH₃C≡N)₂], where L is 3,7,10,11,14,18,21,22-octaazatricyclo[18.2.2.2^{9,12}]hexacos-1(22),2,7,9,11,13,18,20,23,25-decaene (Brooker *et al.*, 1996).

The Cu···Cu distance of 2.9522 (9) Å is rather short for this kind of complex (Rojas *et al.*, 2004). Consistently, the Cu—O—Cu angle is 100.24 (12)°. The atom sequence Cu—O1—Cuⁱ—O1ⁱ is a rather regular parallelogram, with sides of about 1.92 Å. The Cu—O1 and Cu—O1ⁱ distances are 1.923 (3) and 1.920 (3) Å, respectively. The hydroxo H atoms deviate from the Cu₂O₂ plane by 45.5°, a value which might result from packing effects, *i.e.* interaction between the hydroxo H atoms and the O atoms of the perchlorate counter-anion. The distances between atom H1 and the partially occupied perchlorate atoms O5A and O5B are 1.97 and 2.20 Å, respectively. The deviation of the hydroxo H atom from planarity has been described as an important factor which determines the magnetic coupling exchange of binuclear copper(II) complexes (Ruiz *et al.*, 1997).

Experimental

Cu(CH₃C≡N)₄(ClO₄) (1 mmol) was reacted with dibenzyl(6-methyl-2-pyridylmethyl)amine (1 mmol) in moist methanol to give the copper(I) complex which, on reaction with oxygen, afforded the title dinuclear di- μ -hydroxo-dicopper(II) complex. X-ray diffraction quality crystals of (I) were obtained by recrystallization from an acetonitrile–methanol mixture (1:5).

Crystal data

[Cu ₂ (OH) ₂ (C ₂ H ₃ N) ₂ (C ₂₁ H ₂₂ N ₂) ₂](ClO ₄) ₂	$D_x = 1.462 \text{ Mg m}^{-3}$
$M_r = 1046.94$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3378 reflections
$a = 10.1453 (10) \text{ \AA}$	$\theta = 4.6\text{--}46.7^\circ$
$b = 20.0868 (19) \text{ \AA}$	$\mu = 1.07 \text{ mm}^{-1}$
$c = 12.0925 (12) \text{ \AA}$	$T = 571 (2) \text{ K}$
$\beta = 105.193 (2)^\circ$	Prism, blue
$V = 2378.2 (4) \text{ \AA}^3$	$0.55 \times 0.55 \times 0.45 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD area-detector diffractometer	4218 independent reflections
φ and ω scans	3006 reflections with $I > 2\sigma(I)$
Absorption correction: refined on ΔF (SADABS in SAINT-NT; Bruker, 1999)	$R_{\text{int}} = 0.030$
$T_{\text{min}} = 0.572$, $T_{\text{max}} = 0.618$	$\theta_{\text{max}} = 25.1^\circ$
12 077 measured reflections	$h = -11 \rightarrow 12$
	$k = -23 \rightarrow 23$
	$l = -14 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.1158P)^2]$
$wR(F^2) = 0.183$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4218 reflections	$\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
299 parameters	$\Delta\rho_{\text{min}} = -0.74 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—O1 ⁱ	1.920 (3)	Cu—N2	2.070 (3)
Cu—O1	1.923 (3)	Cu—N3	2.476 (5)
Cu—N1	2.044 (3)	Cu—Cu ⁱ	2.9522 (9)
O1 ⁱ —Cu—O1	79.61 (13)	O1 ⁱ —Cu—N3	87.74 (14)
O1 ⁱ —Cu—N1	101.86 (13)	O1—Cu—N3	97.49 (14)
O1—Cu—N1	172.23 (14)	N1—Cu—N3	90.21 (14)
O1 ⁱ —Cu—N2	174.44 (12)	N2—Cu—N3	89.97 (14)
O1—Cu—N2	95.69 (12)	Cu ⁱ —O1—Cu	100.39 (13)
N1—Cu—N2	83.20 (14)	C22—N3—Cu	155.2 (4)

Symmetry code: (i) 1 - x, -y, 2 - z.

During the final stages of refinement, disorder of the perchlorate O atoms was evident. This was modelled considering two partially occupied positions for the perchlorate anion, with occupancy factors of 0.60 and 0.40. All the Cl—O distances were set equal to common parameters, which were refined and finally set at 1.39 and 1.43 Å for the two anions. The H atoms of the amine were introduced in calculated positions and refined using the riding model, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The hydroxo H atom was located by difference synthesis and the coordinates were not subsequently refined.

Data collection: SMART-NT (Bruker, 2001); data reduction: SAINT-NT (Bruker, 1999); 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: AV1222). Services for accessing these data are described at the back of the journal.

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