

The coordination custom customizably customizable customized customizing customisably customisable customized customizing 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 bis-methoxy-bridged copper(II) complex $[\text{Cu}(\text{BiBzMePMA})]_2\text{-}\mu_2(\text{OCH}_3)_2$, which has been fully characterized, both magnetically and structurally (Rojas *et al.*, 2004). Here, we report the crystal structure of the analogous bis-hydroxo-bridged compound, $[\text{Cu}(\text{BiBzMePMA})]_2\text{-}\mu_2(\text{OH})_2$, (I), resulting from the same synthetic procedure, but in the presence of 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], μ_2 -bridged by two hydroxyl 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 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 hydroxyl O atoms [O1 and O1ⁱ; symmetry code: (i) 1 - *x*, -*y*, 2 - *z* Please check added symmetry code], while the acetonitrile atom N3 occupies the apical position. This N atom deviates by 3.7° from the perpendicular to the basal-plane position.

The Cu—N_{acetonitrile} distance is 2.476 (5) Å, a rather long value for this kind of bond, which is usually in the range 2.00–2.50 Å. A shorter value of about 2 Å has been described for $[\text{Cu}_2(\text{L}_2)(\text{CH}_3\text{CN})_2]^{4+}$, where *L* is tetrakis(1-methylimidazol-2-ylmethyl)-2-hydroxy-1,3-diaminopropane (Gentshev *et al.*, 2000), while a distance of 2.322 (6) Å has been described 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 molecule 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 CuO_2Cu 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 $[\text{Cu}_2\text{L}(\text{CH}_3\text{C}\equiv\text{N})_2]$, where *L* is 3,7,10,11,14,18,21,22-octazaatricyclo[18.2.2.2^{9,12}]-hexacosal(22),2,7,9,11,13,18,20,23,25-decaene (Brooker *et al.*, 1996).

The Cu—Cu distance is 2.9522 (9) Å, a rather short value 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 hydroxy H atoms deviate from the Cu—O plane by 45.5°, a value which can be affected by packing effects, *i.e.* interaction between the hydroxy H atoms and the O atoms of the perchlorate counteranion. The distances between atom H1 and the partially occupied perchlorate atoms O5A and O5B are 1.974 and 2.196 Å, respectively. The deviation of the hydroxy 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).

$\text{Cu}(\text{CH}_3\text{C}\equiv\text{N})_4(\text{ClO}_4)$ (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 bis-hydroxo-bridged copper(II) complex. X-ray diffraction quality crystals of (I) were obtained by recrystallization from an acetonitrile–methanol mixture (Ratio?).