

The first di- μ -hydroxo-bridged binuclear copper complex containing a bis-guanidine ligand

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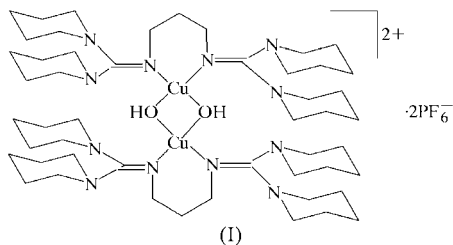
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The present structure determination of di- μ -hydroxo-bis{[*N,N'*-bis(dipiperidinomethylene)propane-1,3-diamine- κ^2N,N']copper(II)} bis(hexafluorophosphate), [Cu₂(OH)₂(C₂₅H₄₆N₆)₂](PF₆)₂, is the first to crystallographically characterize a Cu₂(μ -OH)₂ complex with a bidentate guanidine ligand. The cation lies on a crystallographic inversion centre and shows planar fourfold coordination of the copper centres. The Cu₂(μ -OH)₂ species can be distinguished from Cu₂(μ -O)₂ by the Cu—O bond lengths. The packing is determined by strong intermolecular anion–cation hydrogen bonds.

Comment

The activation of dioxygen by tyrosinase-like Cu^I complexes plays an important role in biological and synthetic oxidation processes. Recent efforts have been directed towards elucidating the structure–reactivity relationship of the underlying Cu₂O₂ species through synthetic model systems (Tolman, 1997; Que & Tolman, 2002). In a search for bifunctional N-atom donor ligands able to stabilize unusually high metal oxidation states, we extended our interests towards guanidine-



type systems (Herres *et al.*, 2004a). The first derivative, the bis-tetramethylguanidinopropylene ligand (btmgp), and its complexes with copper, iron and nickel were investigated with regard to their coordination chemistry (Harmjan, 1997; Waden, 1999; Pohl *et al.*, 2000; Schneider, 2000; Herres, 2002). We have now examined the reaction behaviour of mono- and binuclear copper(I) complexes containing the bis(dipiperidinomethylene)propane-1,3-diamine (DPipG₂p) ligand towards molecular oxygen. The reaction products have been

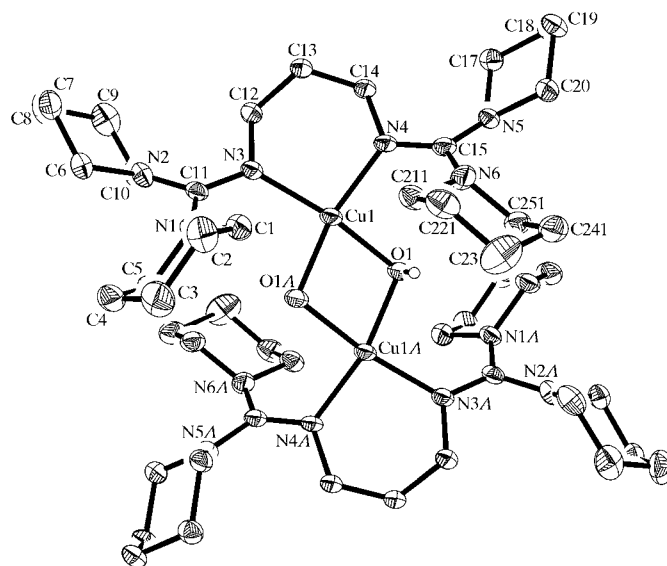


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted and only the major position of the disordered piperidine group at atom N6 is shown. Atoms labelled with the suffix *A* are at the symmetry position ($-x + 1, -y + 1, -z + 1$).

identified as rare examples of alkoxo-bridged binuclear copper complexes, demonstrating that the bidentate ligand has been hydroxylated in an unprecedented manner (Herres *et al.*, 2004b). Another product, the di- μ -hydroxo-bridged binuclear copper title complex, [Cu₂(μ -OH)₂(DPipG₂p)₂](PF₆)₂, (I), will be discussed here.

Selected geometric parameters are given in Table 1. The geometric centre of the cation lies on a crystallographic inversion centre and the resulting Cu₂O₂ core is thus strictly planar. The Cu atom is coordinated in a planar quadrat manner by two guanidine N atoms and the two bridging O atoms. The deviation of the Cu atom from the N₂O₂ plane is 0.036 (1) Å, and the chelate heterocycle adopts a chair conformation. The presence of the hydroxo H atom was confirmed from Fourier maps. The Cu···Cu and mean Cu—O distances [3.0740 (6) and 1.935 (2) Å] are clearly elongated compared with those of di- μ -oxo-bridged Cu₂O₂ moieties, which are in the ranges 2.743 (1)–2.906 (1) and 1.796 (6)–1.865 (3) Å, respectively. Similar observations hold for related Fe complexes (Que & Tolman, 2002). As pointed out by Que & Tolman (2002), the significant differences between the short [in M₂(μ -O)₂] and long [in M₂(μ -OH)₂] M—O distances are obviously a suitable measure for distinguishing between these two species. The N6 piperidine group is disordered over two sites, with occupation factors of 0.823 (6) and 0.177 (6). Fig. 1 displays only the major position. The packing (Fig. 2) is determined by intermolecular hydrogen bonds between the cation and the hexafluorophosphate anions [C14—H14A···F16($-x + 1, -y + 1, -z + 1$), with H···F = 2.28 Å and C—H···F = 170°, C3—H3A···F12, with H···F = 2.38 Å and C—H···F = 161°, and C251—H25A···F15($x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$), with H···F = 2.41 Å and C—H···F = 143°]. The shortest intramolecular interaction is C241—H125D···N6

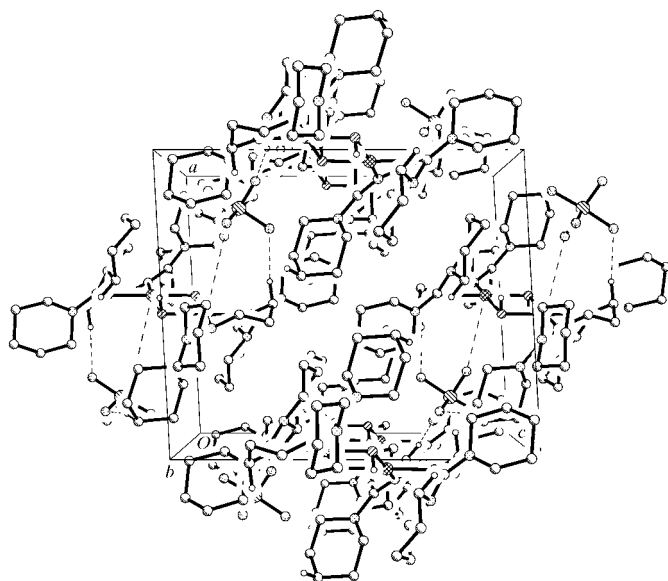


Figure 2
The crystal packing, viewed along [010], with the hydrogen-bonding pattern indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

(H...N = 2.12 Å). All these values are normalized for a C—H distance of 1.08 Å.

Experimental

A solution of [Cu₂(DPipG₂P)₂](PF₆)₂ (262 mg, 0.2 mmol; Herres *et al.*, 2004b) in MeCN (50 ml) was treated at room temperature with pure dioxygen. After the mixture had been left to stand for one week, dark-blue crystals suitable for X-ray diffraction were obtained. IR (KBr, cm⁻¹): 3446 [*ν*_w, *ν*(O—H)], 2937 (*s*), 2852 (*s*), 1533 [*ν*_s, *ν*(C=N)], 1495 [*s*, *ν*(C=N)], 1446 (*vs*), 1371 (*s*), 1335 (*m*), 1253 (*m*), 1226 (*m*), 1205 (*m*), 1164 (*w*), 1141 (*m*), 1110 (*m*), 1070 (*w*), 1020 (*m*), 948 (*m*), 917 (*w*), 839 [*ν*_s, *ν*(P—F)], 744 (*m*), 622 (*w*), 597 (*w*), 557 (*m*), 487 (*w*).

Crystal data

[Cu ₂ (OH) ₂ (C ₂₅ H ₄₆ N ₆) ₂](PF ₆) ₂	<i>D_x</i> = 1.431 Mg m ⁻³
<i>M_r</i> = 1312.39	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cell parameters from 8806 reflections
<i>a</i> = 12.3581 (9) Å	<i>θ</i> = 2.4–28.1°
<i>b</i> = 16.7472 (13) Å	<i>μ</i> = 0.84 mm ⁻¹
<i>c</i> = 14.7430 (11) Å	<i>T</i> = 120 (2) K
<i>β</i> = 93.156 (2)°	Block, blue
<i>V</i> = 3046.6 (4) Å ³	0.40 × 0.35 × 0.25 mm
<i>Z</i> = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	<i>R</i> _{int} = 0.050
<i>φ</i> and <i>ω</i> scans	<i>θ</i> _{max} = 27.9°
Absorption correction: multi-scan (SADABS; Bruker, 2002)	<i>h</i> = -14 → 16
<i>T</i> _{min} = 0.715, <i>T</i> _{max} = 0.810	<i>k</i> = -22 → 22
35 133 measured reflections	<i>l</i> = -19 → 17
7264 independent reflections	8814 standard reflections
4803 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 540 min
	intensity decay: <1%

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0709 <i>P</i>) ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.055	+ 4.1986 <i>P</i>]
<i>wR</i> (<i>F</i> ²) = 0.161	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.03	(Δ/ <i>σ</i>) _{max} = 0.005
7264 reflections	Δ <i>ρ</i> _{max} = 0.97 e Å ⁻³
382 parameters	Δ <i>ρ</i> _{min} = -0.85 e Å ⁻³
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1 ⁱ	1.921 (2)	N2—C11	1.364 (4)
Cu1—O1	1.948 (2)	N3—C11	1.322 (4)
Cu1—N4	1.968 (3)	N4—C15	1.304 (4)
Cu1—N3	1.982 (3)	N5—C15	1.364 (4)
N1—C11	1.362 (4)	N6—C15	1.363 (4)
O1 ⁱ —Cu1—O1	74.78 (11)	O1—Cu1—N3	168.62 (12)
O1 ⁱ —Cu1—N4	166.25 (11)	N4—Cu1—N3	96.02 (11)
O1—Cu1—N4	92.34 (11)	Cu1 ⁱ —O1—Cu1	105.22 (11)
O1 ⁱ —Cu1—N3	97.40 (10)		

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

H atoms attached to C atoms were placed at idealized positions, riding on their attached C atoms, with *U*_{iso}(H) values of 1.2*U*_{eq}(C) and 1.5*U*_{eq}(C_{methyl}). All methyl groups were allowed to rotate but not to tip. The O—H distance of the hydroxo group was restrained to 0.84 (1) Å. The disordered piperidine group at N6 was treated with a split model. Geometric parameters derived for the isotropically refined minor positions are less reliable.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2002); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1771). Services for accessing these data are described at the back of the journal.

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