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Tetrakis(μ-benzoato-κ^2O:O')bis(4-ethylpyridine-κN)-dicopper(II)

Birinchi K. Das,* Sanchay J. Bora and Purabi Sarmah

Department of Chemistry, Gauhati University, Guwahati 781 014, India

Correspondence e-mail: das_bk@rediffmail.com

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The bis(4-ethylpyridine) adduct of dicopper(II) tetrabenzoate, $[Cu_2(C_7H_5O_2)_4(C_7H_9N)_2]$, has centrosymmetrically related square-pyramidal Cu atoms bridged by four benzoate ions; the heterocyclic ligands that occupy the apical sites are disordered.

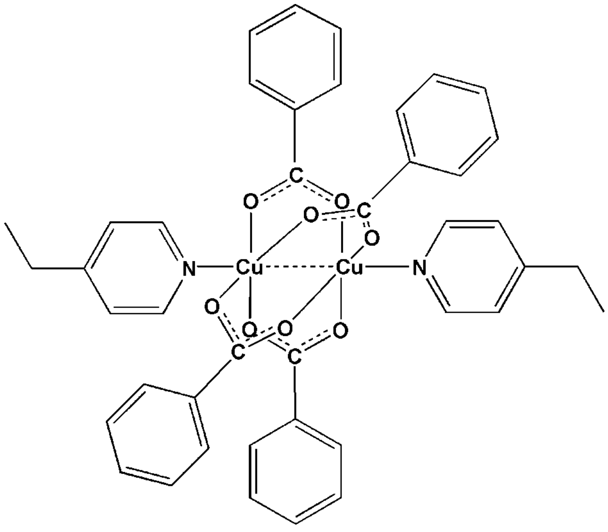
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.145
Data-to-parameter ratio = 22.0

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

Comment

The compound $[Cu_2(CH_3CO_2)_4(H_2O)_2]$ and its structural analogues display interesting magnetic properties (Cotton *et al.*, 1999). We have investigated some compounds of the type $[Cu_2(RCO_2)_4L_2]$, where L is a monodentate pyridine ligand, to evaluate their catalytic properties in reactions including the catalytic oxidation of benzylic and other alcohols. In this connection, we have isolated the 4-ethylpyridine diadduct of dicopper(II) tetrabenzoate in crystalline form.



(I)

The structure of $[Cu_2(\mu\text{-}O_2CC_6H_5)_4(4\text{-Etpy})_2]$, (I) (Fig. 1), is similar to that of copper(II) acetate hydrate (Brown & Chidambaram, 1973). The Cu···Cu atoms are related by a centre of symmetry present at the mid-point of the Cu···Cu axis. The Cu···Cu distance of 2.6714 (6) Å in the title compound is longer than those found in the two forms of $[Cu_2(\mu\text{-}O_2CCH_3)_4(py)_2]$ [2.645 (2) Å (Hanic *et al.*, 1964) and 2.630 (2) Å (Barclay & Kennard, 1961)] as well as that in $[Cu_2(\mu\text{-}O_2CCH_3)_4(4\text{-CNpy})_2]$ [2.600 (1) Å; Das & Barman, 2001]. The Cu—O bond lengths are close to 1.97 Å, but the Cu—N distance is longer, at 2.173 (3) Å. This Cu—N distance is, however, shorter than the corresponding distance of 2.188 (2) Å found for $[Cu_2(\mu\text{-}O_2CCH_3)_4(4\text{-CNpy})_2]$. This

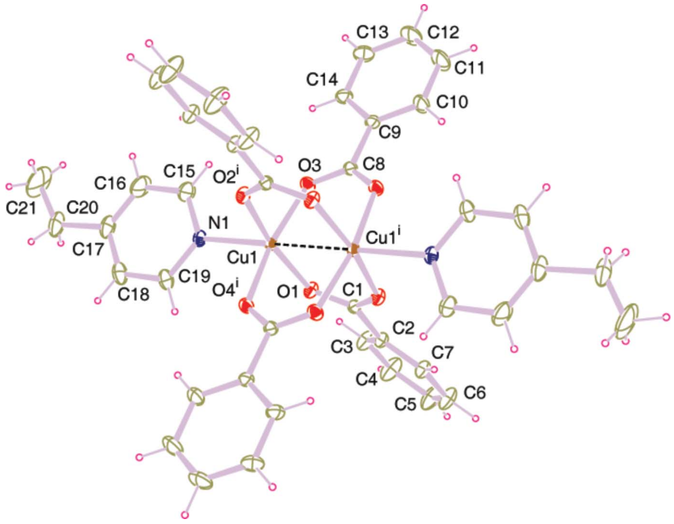


Figure 1
The molecular structure of (I), showing 20% probability displacement ellipsoids.

shortening of the Cu—N(pyridyl) distance may reflect the inductive effects of the substituent groups present at the 4-positions of the pyridine ligands. The long Cu—*L*(apical ligands) distance is characteristic of $[Cu_2(CH_3CO_2)_4L_2]$-type structures (Catterick & Thornton, 1977). The distorted nature of the CuO_4N square pyramid can be seen from the O—Cu—O and O—Cu—N angles (Table 1). While the former are found to be in the range 88.24 (9)–167.30 (8)°, the latter are in the range 91.76 (13)–100.94 (13)°. The Cu atom lies 0.1746 (8) Å, towards the coordinated N atom, from the mean plane formed by the four basal O atoms.

The 4-ethylpyridine ligands present at the apical sites are orientationally disordered over two sites. The least-squares planes defined by N1, C15, C16, C17, C18, C19 and C20 for the principal component [occupancy = 0.676 (5)] and by N1′, C15′, C16′, C17′, C18′, C19′ and C20′ for the minor component [occupancy = 0.324 (5)] make a dihedral angle of 43.5(6)°.

Experimental

Cupric chloride dihydrate (1 mmol) was taken in 25 ml of methanol. To this, sodium benzoate (2 mmol) was added and the mixture was stirred at room temperature for *ca* 10 min. To the green solution 4-ethylpyridine (1 mmol) was then added and stirring was continued for 1 h. The resulting green precipitate was filtered off, washed with methanol and dried in air to obtain a green powder. Yield 90%. Single crystals suitable for X-ray diffraction were obtained from a methanol solution of the title complex by slow evaporation.

Crystal data

$[Cu_2(C_7H_5O_2)_4(C_7H_9N)_2]$
M_r = 825.82
Monoclinic, $P2_1/n$
a = 10.2298 (2) Å
b = 10.9739 (2) Å
c = 17.5785 (4) Å
β = 94.737 (1)°
V = 1966.64 (7) Å^3
Z = 2
D_x = 1.395 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.14 mm^{-1}
T = 293 (2) K
Block, green–blue
0.44 × 0.34 × 0.22 mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 2004)
T_{min} = 0.635, T_{max} = 0.788
16781 measured reflections
4868 independent reflections
3765 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.145
S = 1.05
4868 reflections
221 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 0.8035P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.9644 (19)	Cu1—O1	1.972 (2)
Cu1—O2^i	1.9686 (19)	Cu1—N1	2.173 (3)
Cu1—O4^i	1.971 (2)	Cu1···Cu1^i	2.6714 (6)
O3—Cu1—O1	89.42 (10)	O1—Cu1—N1	100.94 (13)
O3—Cu1—N1	99.37 (14)		

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

All H atoms were placed at calculated positions (C—H = 0.93–0.97 Å) and treated as riding [$U_{iso}(H) = xU_{eq}(C)$, where x = 1.2 or 1.5]. The disordered $-NC_5H_4$-4-C_2H_5 (4-Etpy) group was refined using geometrical restraints. Disordered components of each atom were refined with identical displacement parameters, and the two occupancy factors refined to 0.676:0.324 (5).

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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