

μ_4 -Oxo-hexa- μ_2 -chloro-tetrakis[(benzimidazole- κN)copper(II)] ethanol disolvate: a reformulation**Yun-Qian Zhang,^a Duan-Jun Xu^{b*} and Jian-Rong Su^b**^aDepartment of Chemistry, Zhejiang University, People's Republic of China, and Department of Chemistry, Guizhou University, People's Republic of China, and ^bDepartment of Chemistry, Zhejiang University, People's Republic of China

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Key indicators

Single-crystal X-ray study

T = 298 K

Mean $\sigma(C-C)$ = 0.012 Å

H-atom completeness 84%

Disorder in solvent or counterion

R factor = 0.051

wR factor = 0.185

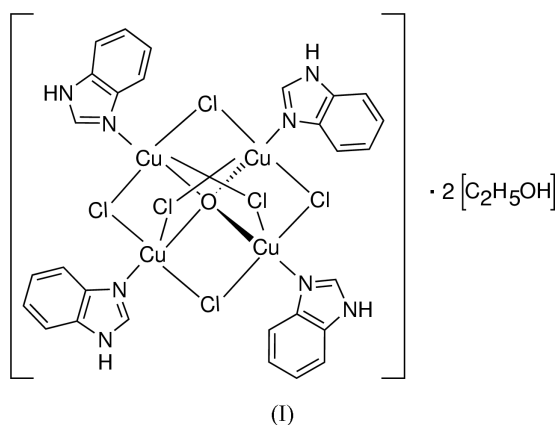
Data-to-parameter ratio = 20.1

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

The title compound $[Cu_4Cl_6O(C_7H_6N_2)_4] \cdot 2C_2H_5OH$, consists of the tetranuclear copper(II) complex and uncoordinated ethanol molecules. The structure was reported previously by Tosik, Bukowska-Strzyzewska & Mrozinski [*J. Coord. Chem.* (1991), **24**, 113–120], but only 0.68 ethanol molecules were found in the asymmetric unit. The present redetermination indicates that two ethanol molecules occur in the asymmetric unit. One ethanol molecule is ordered while the other one is disordered, with the hydroxyl group in two alternative sites. Both disordered hydroxyl groups hydrogen bond to the ordered ethanol molecule with O \cdots O separations of 2.845 (16) and 2.67 (2) Å, and O–H \cdots O angles of 156 and 147°, respectively.

Comment

Crystals of the title compound, (I), were occasionally obtained as a by-product in the preparation of a complex of (4-hydroxybenzoato)copper(II) with benzimidazole.



The molecular structure of (I) is illustrated in Fig. 1. There are one tetranuclear copper(II) complex and two ethanol molecules in the asymmetric unit. The structure of the copper(II) complex is the same as that reported previously (Tosik *et al.*, 1991). One ordered ethanol molecule, which was ignored in the previous determination, hydrogen bonds to a benzimidazole of the adjacent copper(II) complex (Fig. 1 and Table 2). The other ethanol molecule is disordered in the structure, the hydroxyl group located in different sites with site-occupancy factors of 0.68 (O3a) and 0.32 (O3b), respectively. Atom O3b was ignored in the previous determination. As shown in Fig. 1, both O3a and O3b hydrogen bond to the ordered ethanol, with reasonable O \cdots O separations and O–H \cdots O angles (Table 2). The H atoms on the disordered

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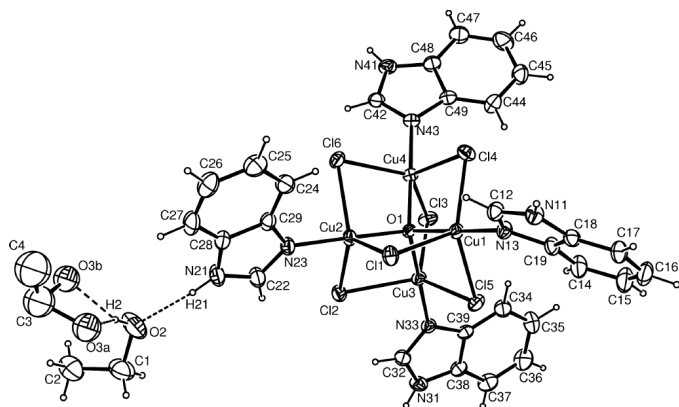


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. Dashed lines indicate hydrogen bonds. The suffixes *a* and *b* indicate the disordered hydroxyl groups.

ethanol molecule were not located in the structure, but the separation of 2.60 (3) Å suggests the existence of intermolecular hydrogen bonding between atoms O3b and O3b(2 - *x*, 2 - *y*, 2 - *z*).

Experimental

Sodium 3-hydroxybenzoate (0.16 g, 1 mmol), benzimidazole (0.12 g, 1 mmol) and CuCl₂·2H₂O (0.17 g, 1 mmol) were dissolved in absolute ethanol (15 ml). The solution was refluxed for 5 h and a red precipitate appeared. After cooling to room temperature, the solution was filtered. Brown crystals were obtained from the filtrate after 5 d.

Crystal data

[Cu₄Cl₆O(C₇H₆N₂)₄]·2C₂H₆O
M_r = 1047.55
 Triclinic, P1
a = 13.0005 (14) Å
b = 13.2362 (15) Å
c = 13.8867 (9) Å
 α = 68.062 (2)°
 β = 74.315 (2)°
 γ = 71.376 (2)°
V = 2069.2 (4) Å³

Z = 2
D_x = 1.681 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 10395 reflections
 θ = 3.0–26.0°
 μ = 2.46 mm⁻¹
T = 298 (2) K
 Prism, brown
 0.41 × 0.21 × 0.11 mm

Data collection

Rigaku R-AXIS-RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.358, *T_{max}* = 0.758
 19494 measured reflections

9365 independent reflections
 6936 reflections with *I* > 2σ(*I*)
R_{int} = 0.034
 θ_{max} = 27.5°
h = -16 → 16
k = -17 → 17
l = -18 → 16

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.051
wR (*F*²) = 0.185
S = 0.86
 9365 reflections
 467 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.1372*P*)² + 6.2288*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 1.01 e Å⁻³
 Δρ_{min} = -0.89 e Å⁻³

Table 1
Selected geometric parameters (Å).

Cu1—O1	1.905 (3)	Cu3—O1	1.908 (3)
Cu1—N13	1.955 (4)	Cu3—N33	1.947 (4)
Cu1—Cl4	2.3538 (15)	Cu3—Cl5	2.3833 (15)
Cu1—Cl5	2.4068 (15)	Cu3—Cl3	2.4331 (15)
Cu1—Cl1	2.5095 (14)	Cu3—Cl2	2.4436 (15)
Cu2—O1	1.923 (3)	Cu4—O1	1.916 (3)
Cu2—N23	1.957 (4)	Cu4—N43	1.948 (4)
Cu2—Cl1	2.3958 (15)	Cu4—Cl3	2.3629 (15)
Cu2—Cl6	2.4435 (16)	Cu4—Cl6	2.4231 (14)
Cu2—Cl2	2.4571 (15)	Cu4—Cl4	2.4596 (15)

Table 2
Hydrogen-bonding 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>
O2—H2···O3a	0.87	2.03	2.845 (16)	156
O2—H2···O3b	0.87	1.88	2.67 (2)	147
N11—H11···Cl6 ⁱ	0.86	2.70	3.445 (6)	146
N21—H21···O2	0.86	1.96	2.761 (10)	155
N31—H31···Cl1 ⁱⁱ	0.86	2.59	3.372 (5)	152
N41—H41···Cl2 ⁱⁱⁱ	0.86	2.69	3.408 (5)	141

Symmetry codes: (i) 2 - *x*, 1 - *y*, 1 - *z*; (ii) 1 - *x*, 1 - *y*, 2 - *z*; (iii) 1 - *x*, 2 - *y*, 1 - *z*.

The disordered ethanol molecule was refined isotropically, and its H atoms were not located. The hydroxyl H atom of the ordered ethanol was placed in a calculated position (Nardelli, 1999), and included in the final cycles of refinement with fixed coordinates and an isotropic displacement parameter of 0.10 Å². Other H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and included in the final cycles of refinement in a riding model, with *U*_{iso}(H) = 1.2*U*_{eq} or 1.5*U*_{eq} of the carrier atoms. The peak with the maximum electron density in the difference Fourier map was close (0.87 Å) to atom C3.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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