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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$   
 $R$  factor = 0.069  
 $wR$  factor = 0.130  
Data-to-parameter ratio = 10.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A tetranuclear copper complex,  
[Cu<sub>4</sub>( $\mu_3$ -OH)<sub>2</sub>( $\mu_2$ -OH)<sub>2</sub>(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O

The crystal structure of the title compound, diaquadi- $\mu_3$ -hydroxo-di- $\mu_2$ -hydroxo-tetraphenanthroline-tetracopper(II) tetranitrate dihydrate, [Cu<sub>4</sub>(OH)<sub>4</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O, was determined by single-crystal X-ray diffraction. The tetranuclear copper structure has a chair form and each copper has a tetragonal pyramidal coordination geometry. The compound was synthesized by the hydro-(solvo)thermal method and there is a fluorescence peak at 450 nm.

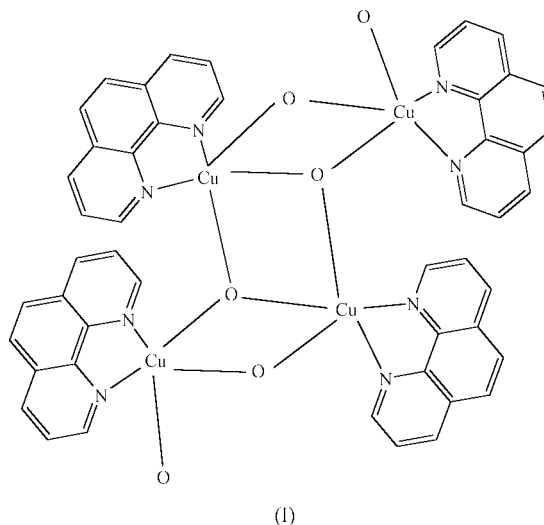
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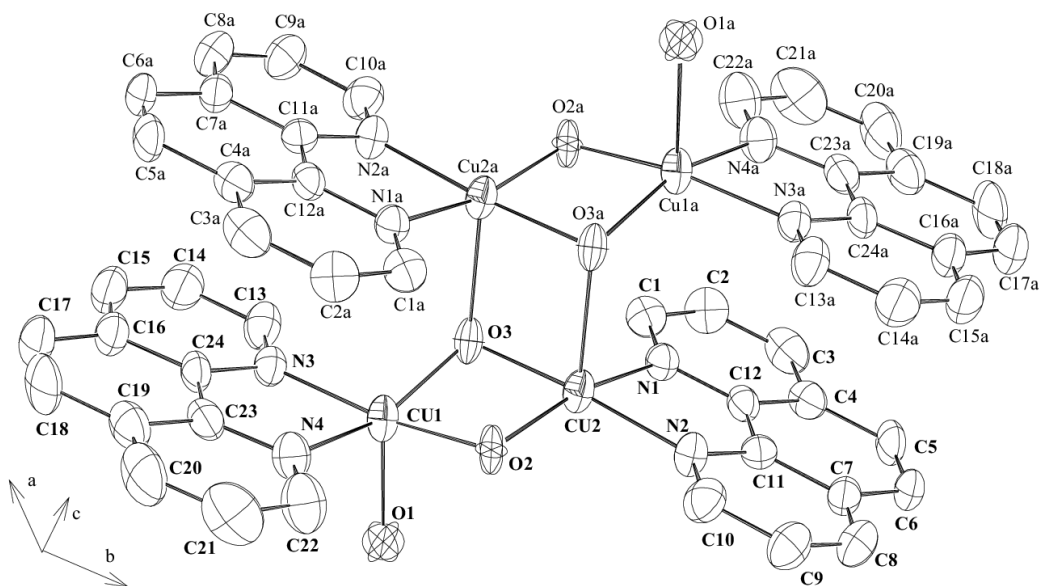
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## Comment

Current research work on the structures, fluorescence and magnetic properties of polynuclear transition metal compounds is aimed at understanding the structural and chemical features governing electronic exchange coupling through multiatom bridging ligands. Although the greatest effort and success have been in the study of dinuclear Cu<sup>2+</sup> complexes, there has been little work on oligomeric copper complexes with more than two copper ions (Gutierrez *et al.*, 2000), particularly on chair form tetranuclear copper complexes connected by  $\mu$ -hydroxo which have generally been observed as central bridging ligands (Ferrer *et al.*, 2000). We report here a chair-form tetranuclear copper complex, [Cu<sub>4</sub>( $\mu_3$ OH)<sub>2</sub>( $\mu_2$ OH)<sub>2</sub>(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O (phen is phenanthroline), (I).



The cation structure of the title compound is shown in Fig. 1. In the chair-form tetranuclear copper structure, each copper has a tetragonal pyramidal coordination geometry. The bond lengths from the  $\mu_2$ -O atoms (O2 and O2a) to Cu atoms are shorter than those from the  $\mu_3$ -O atoms (O2 and O2a) to Cu



**Figure 1**

The cationic structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity.

(Cu1, Cu2 and Cu2a, Cu1a) atoms. In particular, the bond lengths O1—Cu2a and O2—Cu2 are 2.322 (19) and 2.34 (2) Å, respectively. Selected bond lengths and bond angles are listed in Table 1. The two 1,10-phenanthroline molecules coordinating with Cu1 and Cu2 are almost coplanar and the two pairs of 1,10-phenanthroline molecules are parallel. The Cu1—Cu2 and Cu2—Cu2a distances are 2.919 and 2.926 Å, respectively. The short metal–metal bond distance may permit a direct interaction or the spin–spin coupling may be accomplished by a super-exchange mechanism (Carlin, 1969).

## Experimental

The title compound was synthesized by the hydro(solvo)thermal method. 0.5 g  $\text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ , 0.2 g 1,10-phenanthroline and 6 ml  $\text{H}_2\text{O}$  were added to a 25 ml Teflon-lined Parr autoclave. The autoclave was sealed and heated under static conditions for 96 h at 443 K; the reaction was cooled to room temperature over a period of 50 h.

### Crystal data

$[\text{Cu}_4(\text{OH})_4(\text{C}_{10}\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$	$Z = 1$
$M_r = 1355.04$	$D_x = 1.715 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.1504 (1) \text{ \AA}$	Cell parameters from 47 reflections
$b = 11.9299 (3) \text{ \AA}$	$\theta = 1.8\text{--}25.0^\circ$
$c = 12.6337 (1) \text{ \AA}$	$\mu = 1.69 \text{ mm}^{-1}$
$\alpha = 111.073 (1)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 90.906 (2)^\circ$	Cube, blue
$\gamma = 111.218 (2)^\circ$	$0.30 \times 0.18 \times 0.12 \text{ mm}$
$V = 1311.91 (4) \text{ \AA}^3$	

### Data collection

Siemens SMART CCD diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.597$ ,  $T_{\max} = 0.816$   
 6772 measured reflections

4544 independent reflections  
 2762 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$   
 $\theta_{\max} = 25.0^\circ$   
 $h = -12 \rightarrow 7$   
 $k = -14 \rightarrow 14$   
 $l = -14 \rightarrow 15$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.069$   
 $wR(F^2) = 0.130$   
 $S = 1.39$   
 4544 reflections  
 440 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.008$   
 $\Delta\rho_{\max} = 0.76 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.57 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O2	1.922 (4)	Cu2—O2	1.924 (4)
Cu1—O3	1.977 (6)	Cu2—O3	1.966 (6)
Cu1—N4	2.022 (6)	Cu2—N2	2.013 (5)
Cu1—N3	2.022 (5)	Cu2—N1	2.029 (5)
Cu1—O1	2.235 (4)	Cu2—O3 <sup>i</sup>	2.318 (6)
Cu1—Cu2	2.9191 (10)	O3—Cu2 <sup>i</sup>	2.318 (6)
O2—Cu1—O3	81.9 (2)	O3—Cu2—N1	97.7 (2)
O2—Cu1—N4	95.8 (2)	N2—Cu2—N1	81.9 (2)
O3—Cu1—N4	157.3 (2)	O2—Cu2—O3 <sup>i</sup>	101.9 (2)
O2—Cu1—N3	169.30 (19)	O3—Cu2—O3 <sup>i</sup>	83.7 (3)
O3—Cu1—N3	96.5 (2)	N2—Cu2—O3 <sup>i</sup>	101.4 (2)
N4—Cu1—N3	81.6 (2)	N1—Cu2—O3 <sup>i</sup>	93.6 (2)
O2—Cu1—O1	95.62 (17)	O2—Cu2—Cu1	40.60 (11)
O3—Cu1—O1	102.1 (2)	O3—Cu2—Cu1	42.39 (18)
N4—Cu1—O1	100.7 (2)	N2—Cu2—Cu1	135.62 (17)
N3—Cu1—O1	95.06 (18)	N1—Cu2—Cu1	134.52 (15)
O2—Cu1—Cu2	40.65 (13)	O3 <sup>i</sup> —Cu2—Cu1	100.32 (13)
O3—Cu1—Cu2	42.09 (17)	C1—N1—C12	117.8 (6)
N4—Cu1—Cu2	135.16 (16)	C1—N1—Cu2	129.8 (4)
N3—Cu1—Cu2	138.57 (17)	C12—N1—Cu2	112.1 (4)
O1—Cu1—Cu2	95.07 (12)	Cu1—O2—Cu2	98.75 (19)
O2—Cu2—O3	82.1 (2)	Cu2—O3—Cu1	95.5 (3)
O2—Cu2—N2	96.9 (2)	Cu2—O3—Cu2 <sup>i</sup>	96.3 (3)
O3—Cu2—N2	174.9 (2)	Cu1—O3—Cu2 <sup>i</sup>	111.9 (3)
O2—Cu2—N1	164.44 (19)		

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

Data collection: SMART (Siemens, 1998); cell refinement: SMART; data reduction: SAINT (Siemens, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

*SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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