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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.045

wR factor = 0.115

Data-to-parameter ratio = 11.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Di- μ -hydroxo-bis[aqua(1,10-phenanthroline- κ^2N,N')copper(II)] dinitrate hexahydrate

The title compound, $[\text{Cu}_2(\text{OH})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, consists of a hydroxo-bridged dinuclear complex dication, two nitrate anions and six water molecules arranged around an inversion center. The $\text{Cu} \cdots \text{Cu}$ distance is $2.902(1) \text{ \AA}$. The packing is governed by an intricate $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bond network and also by $\pi-\pi$ interactions.

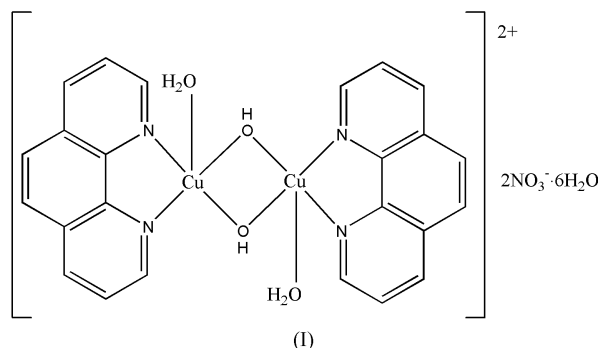
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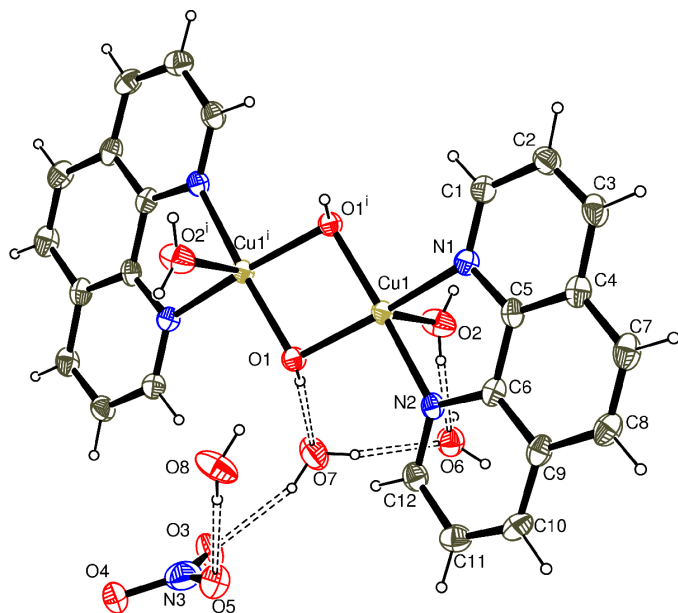
Comment

Copper–1,10-phenanthroline (phen) complexes have attracted much attention because of their structural complexity. Recently, a variety of copper–phen complexes with diverse structures have been studied, especially multi-nuclear copper–phen complexes (Zhang *et al.*, 2002; Lu *et al.*, 2004; Zheng *et al.*, 2001; Li *et al.*, 2000). We report here the crystal structure of the title compound, (I).



The molecular structure is illustrated in Fig. 1. The compound consists of a divalent $[\text{Cu}_2(\text{phen})_2(\text{OH})_2(\text{H}_2\text{O})_2]$ complex cation, two nitrate anions and six water molecules arranged around an inversion center. In the complex cation, the Cu^{2+} environment is that of a distorted square pyramid composed of two phen N atoms and two O atoms of bridging hydroxide at the corners of the basal square and a fifth weakly coordinated water molecule at the apical position. Two adjacent square pyramids ($\text{CuN}_2\text{O}_2\text{Ow}$) are condensed *via* two μ -OH groups to form a dinuclear complex cation. This structure differs very little from those described previously (Zheng *et al.*, 2000; Lu *et al.*, 2003). However, the $\text{Cu} \cdots \text{Cu}$ distance is shorter than that in $[\text{Cu}_2(\text{phen})_2(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2(\text{phen})_2(\text{OH})_2\text{Cl}_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, and the $\text{Cu}-\text{O}(\text{water})$ bond is shorter than in both reported compounds (see Table 3).

The hydrogen-bonding geometry in (I) is listed in Table 2 and illustrated in Figs. 1 and 2. The nitrate anions, coordinated water molecules and μ -OH groups are connected by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds *via* water molecules, giving rise to an intricate $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bond network. The crystal

**Figure 1**

The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x, y, z$.]

structure is also stabilized by π - π interactions, with a phen-phen separation of 3.45 Å.

Experimental

Chemicals were commercially available (reagent grade) and used without further purification. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.2416 g, 1.0 mmol) was dissolved in water (30 ml) and stirred at room temperature. To this solution was added, dropwise, 1,10-phenanthroline monohydrate (0.198 g, 1.0 mmol) dissolved in water (10 ml) with a few drops of 1.0 M hydrochloric acid; the solution became green under continuous stirring for 20–30 min; its pH was then adjusted to 11 using 1.0 M potassium hydroxide solution and the solution turned blue. The solution was filtered and the filtrate kept at room temperature. Blue crystals were obtained from the basic solution after one month, by slowly evaporating the water solvent. Analysis found: C 36.50, H 4.34, N 10.65%; calculated for $\text{C}_{24}\text{H}_{34}\text{Cu}_2\text{N}_6\text{O}_{16}$: C 36.32, H 4.40, N 10.19%.

Crystal data

$[\text{Cu}_2(\text{OH})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot \text{softretun}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

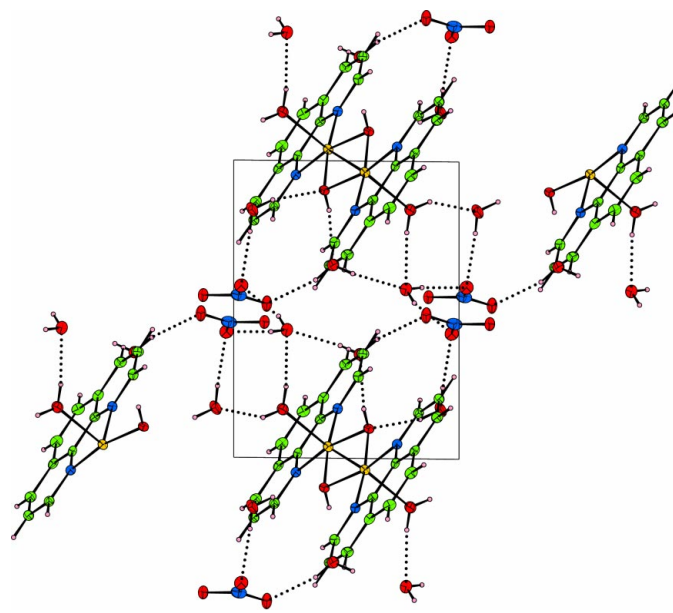
$M_r = 789.65$
Triclinic, $P\bar{1}$
 $a = 8.078$ (2) Å
 $b = 9.604$ (2) Å
 $c = 10.480$ (3) Å
 $\alpha = 81.145$ (3)°
 $\beta = 88.341$ (4)°
 $\gamma = 75.731$ (3)°
 $V = 778.4$ (3) Å³

$Z = 1$
 $D_x = 1.684$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1793 reflections
 $\theta = 2.6$ – 26.8 °
 $\mu = 1.45$ mm⁻¹
 $T = 173$ (2) K
Block, blue
 $0.25 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.699$, $T_{\max} = 0.745$
3804 measured reflections

2687 independent reflections
2359 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 25.0$ °
 $h = -9 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -11 \rightarrow 12$

**Figure 2**

The hydrogen-bond (dashed lines) network of (I), viewed along the b axis.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.115$
 $S = 1.02$
2687 reflections
244 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0703P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.80$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.61$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O1 ⁱⁱ	1.935 (2)	Cu1—N2	2.025 (3)
Cu1—O1	1.944 (2)	Cu1—O2	2.237 (3)
Cu1—N1	2.019 (3)	Cu1—Cu1 ⁱⁱ	2.9018 (9)
O1 ⁱⁱ —Cu1—O1	83.14 (10)	N1—Cu1—N2	81.81 (11)
O1 ⁱⁱ —Cu1—N1	96.36 (11)	O1 ⁱⁱ —Cu1—O2	96.44 (11)
O1—Cu1—N1	166.59 (11)	O1—Cu1—O2	94.59 (11)
O1 ⁱⁱ —Cu1—N2	171.68 (12)	N1—Cu1—O2	98.77 (12)
O1—Cu1—N2	96.75 (11)	N2—Cu1—O2	91.86 (12)

Symmetry code: (ii) $1 - x, 2 - y, 2 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots O7	0.80 (4)	2.01 (2)	2.789 (4)	166 (4)
O2—H2C \cdots O6	0.80 (4)	2.02 (2)	2.809 (4)	170 (4)
O2—H2B \cdots O8 ⁱⁱⁱ	0.80 (4)	2.00 (3)	2.713 (4)	149 (4)
O6—H6A \cdots O5 ^{iv}	0.80 (4)	1.99 (2)	2.761 (4)	160 (4)
O6—H6B \cdots O5 ⁱⁱⁱ	0.83 (3)	1.92 (2)	2.738 (4)	168 (4)
O7—H7B \cdots O3	0.81 (4)	2.05 (2)	2.829 (4)	160 (4)
O7—H7A \cdots O6	0.81 (4)	1.99 (2)	2.784 (4)	169 (5)
O8—H8A \cdots O5	0.81 (4)	2.000 (18)	2.809 (4)	176 (4)
O8—H8B \cdots O1	0.81 (4)	1.95 (2)	2.737 (4)	164 (4)

Symmetry codes: (iii) $1 + x, y, z$; (iv) $1 - x, 2 - y, 1 - z$.

Table 3

Comparison of Cu—Cu and Cu—O distances (Å) within the cations for related structures.

Anion	Cu—Cu	Cu—O(OH)	Cu—O(OH)	Cu—O(H ₂ O)	Reference
NO ₃ [−]	2.902 (1)	1.935 (2)	1.944 (2)	2.235 (3)	<i>a</i>
HCO ₃ [−]	2.905 (1)	1.941 (1)	1.949 (1)	2.254 (2)	<i>b</i>
Cl [−]	2.933 (1)	1.925 (1)	1.949 (1)	2.347 (2)	<i>c</i>

References: (a) this work; (b) Zheng *et al.* (2000); (c) Lu *et al.* (2003).

H atoms attached to C atoms were positioned geometrically, with $C_{sp^2}-H = 0.95$ Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms on O atoms of solvent water were located in difference Fourier maps and their overall U_{iso} value was refined. The O—H distances are in the range 0.80–0.83 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 1999).

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