

Bis(μ -1,10-phenanthrolin-2-olato- κ^3N,N',O)dicopper(I)(Cu—Cu) monohydrate

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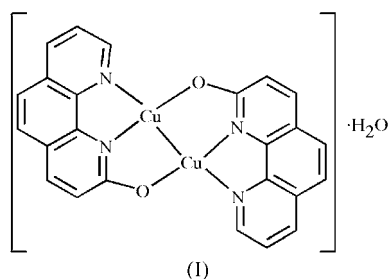
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The crystal structure of the title compound, $[\text{Cu}_2(\text{C}_{12}\text{H}_7\text{N}_2\text{O})_2] \cdot \text{H}_2\text{O}$, shows that this dinuclear complex has shorter Cu—N, Cu—O and Cu—Cu distances within the coordination sphere than similar reported complexes. The complex molecule is located on a centre of symmetry and the water molecule is on a twofold axis of the space group $C2/c$. The discrete complex molecules are extended into a two-dimensional supramolecular array *via* π – π stacking interactions, intermolecular Cu \cdots Cu interactions and C—H \cdots O hydrogen bonds.

Comment

The copper(II) complex of 1,10-phenanthroline (phen), the first artificial nuclease, has been well investigated over the past two decades. Although $[(\text{phen})_2\text{Cu}]^+$ or $[(\text{phen})_2\text{Cu}_2]^+$ are thought to be the active species for DNA cleavage (Sigman *et al.*, 1993; Lu *et al.*, 2003), it is still not known how these complexes bind to DNA. Therefore, investigating the structures of $[(\text{phen})_2\text{Cu}]^+$ and $[(\text{phen})_2\text{Cu}_2]^+$ would be helpful for



understanding the binding mode. Recently, three supramolecular isomers of dinuclear copper(I) 2-hydroxy-1,10-phenanthroline (Hopen) complexes, $[\text{Cu}_2(\text{o phen})_2]$, synthesized from 1,10-phenanthroline were studied by Zhang, Tong *et al.* (2002). In our experiments, we have obtained a similar complex, the title compound, (I), and we report its crystal structure here.

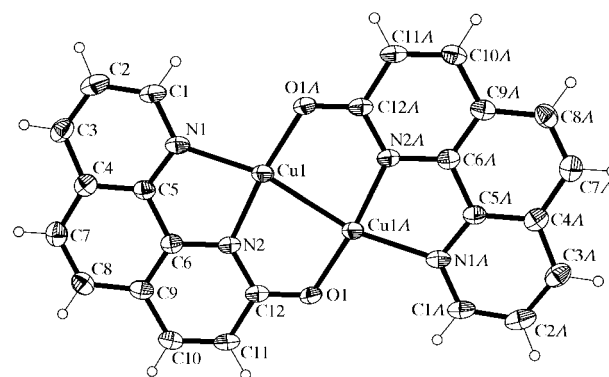


Figure 1

The structure of (I), with displacement ellipsoids drawn at the 30% probability level. Atoms labelled with the suffix *A* are at the symmetry position $(\frac{1}{2} - x, \frac{3}{2} - y, 2 - z)$.

The geometric parameters of (I) are listed in Table 1 and the molecular conformation is illustrated in Fig. 1. The compound contains a $[\text{Cu}_2(\text{oxo-phen})_2]$ complex and a water molecule. The complex molecule is located on a centre of symmetry and the water molecule is on a twofold axis of the space group $C2/c$. Each Cu^+ ion adopts a square-planar geometry, being coordinated by two N atoms from one ophen ligand and one O atom from another ophen ligand, as well as by a second Cu atom. This structure is not much different from that reported by Zhang, Tong *et al.* (2002). However, all coordination bonds around the Cu atoms are shorter than the corresponding bonds [Cu—N = 1.953 (5)–2.274 (6) Å, Cu—O = 1.916 (5)–1.923 (5) Å and Cu—Cu = 2.661 (2)–2.679 (3) Å] in $[\text{Cu}_2(\text{ophen})_2]$ supramolecular isomers, especially the Cu—Cu distance, which is shorter by 0.164–0.182 Å, but much closer to the values observed in mixed-valence $\text{Cu}^+/\text{Cu}^{2+}$ complexes [Cu—Cu = 2.402 (1)–2.443 (2) Å; Zhang, Tong *et al.*, 2002; Zhang, Tong & Chen, 2002]. Thus, the coordination sphere of (I) is tighter and the interaction of both Cu^+ ions is stronger.

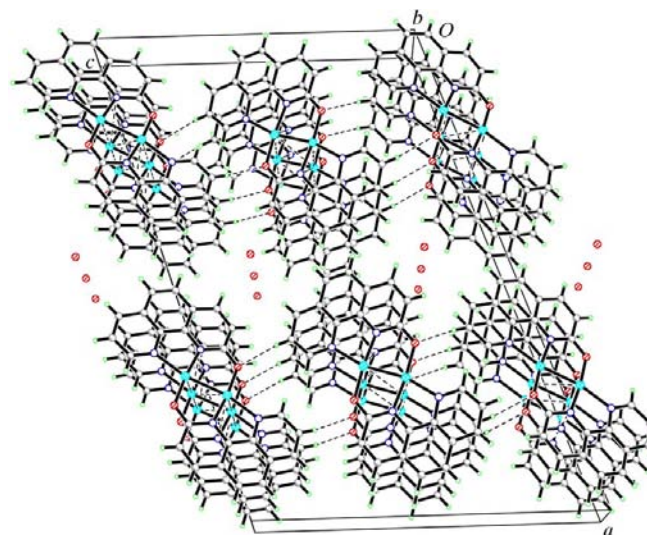


Figure 2

The two-dimensional supramolecular array of (I). Dashed lines between cross-hatched spheres represent Cu \cdots Cu interactions and the remaining dashed lines indicate hydrogen bonds.

The hydrogen-bonding geometry in (I) is listed in Table 2 and illustrated in Fig. 2. In the crystal packing, aromatic π - π stacking interactions are present between the ligand rings of the complex packed along y . These can be best described by considering the C6/C9–C12/N2 ring at (x, y, z) and the C4–C9 ring at $(x, y - 1, z)$, with a centroid–centroid distance of 3.587 (7) Å. The weighted least-squares planes through these two rings are very nearly parallel, as the dihedral angle they form is only 0.40 (13)°. The interplanar spacing is 3.28 (5) Å and the centroid shift is 1.45 (11) Å. Along y , the shortest Cu···Cu contact is $b = 3.6676$ (3) Å. The coordination planes through atoms Cu1/N1/N2/O1 at (x, y, z) and the equivalent atoms at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$ form a dihedral angle of 48.03 (13)°. This is the direction along which the complex molecules are joined *via* weak C–H···O hydrogen-bond interactions (Table 2), giving rise to a zigzag chain that, together with the π - π stacking and Cu···Cu interactions, generates a supramolecular two-dimensional array extended along the length of the crystal.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China; they were used without further purification. Cu(NO₃)₂·3H₂O (0.12 g), 1,10-phenanthroline (0.117 g), 4-aminobenzoic acid (0.034 g) and NaOH (0.02 g) were mixed with water (10 ml) and stirred at room temperature for 30 min. The mixture was then sealed in air and heated at 443 K for 6 d in a 30 ml Teflon-lined autoclave. After cooling, black crystals of (I) were collected.

Crystal data

[Cu ₂ (C ₁₂ H ₇ N ₂ O) ₂] ₂ ·H ₂ O	$D_x = 1.751 \text{ Mg m}^{-3}$
$M_r = 535.49$	Mo $K\alpha$ radiation
Monoclinic, C_2^2/c	Cell parameters from 1851 reflections
$a = 30.344$ (3) Å	$\theta = 2.2$ – 23.7°
$b = 3.6676$ (3) Å	$\mu = 2.13 \text{ mm}^{-1}$
$c = 19.1508$ (17) Å	$T = 293$ (2) K
$\beta = 107.578$ (1)°	Plate, black
$V = 2031.7$ (3) Å ³	$0.28 \times 0.15 \times 0.04 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	1780 independent reflections
φ and ω scans	1506 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.587$, $T_{\text{max}} = 0.920$	$\theta_{\text{max}} = 25.0^\circ$
6470 measured reflections	$h = -36 \rightarrow 35$
	$k = -4 \rightarrow 4$
	$l = -22 \rightarrow 22$

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	1.883 (3)	Cu1–N1	2.109 (4)
Cu1–N2	1.913 (4)	Cu1–Cu1 ⁱ	2.4971 (11)
O1–Cu1–N2	173.36 (16)	N2–Cu1–N1	82.57 (16)
O1–Cu1–N1	104.07 (15)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 2 - z$.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.061$	$w = 1/[\sigma^2(F_o^2) + (0.143P)^2]$
$wR(F^2) = 0.198$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1780 reflections	$\Delta\rho_{\text{max}} = 1.48 \text{ e \AA}^{-3}$
150 parameters	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2–H2···O1 ⁱⁱ	0.93	2.52	3.448 (7)	173

Symmetry code: (ii) $x, 1 - y, z - \frac{1}{2}$.

The residual electron density had a maximum located 0.85 Å from atom O1W. H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^2-H = 0.93$ Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. The water O atom is on a twofold axis, so one H atom is related to the other by symmetry. A peak was found 0.85 Å from the O atom but it forms an unacceptable angle of 150° with its symmetry-related equivalent. On the other hand, the O atom is affected by a rather large U_{eq} value of 0.380 (14) Å², indicative of disorder, the probable cause of which is the lack of hydrogen-bonding interactions involving this water molecule, which is simply occluded in a hole in the structure. For these reasons, the water H atoms were not considered in the present refinement.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: SHELXTL/PC.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1661). Services for accessing these data are described at the back of the journal.

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