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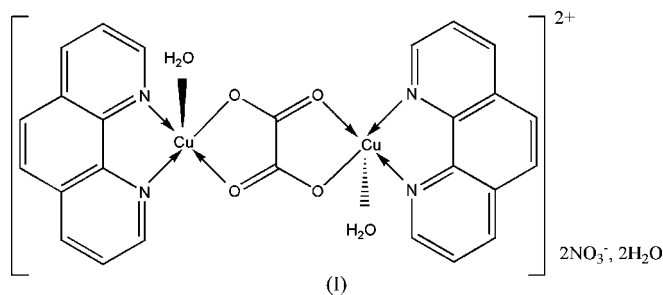
Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.029
 wR factor = 0.084
Data-to-parameter ratio = 13.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>. μ_2 -Oxalato- $\kappa^2\text{O},\text{O}':\kappa^2\text{O}'',\text{O}'''$ -bis[aqua(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$)copper(II)] dinitrate dihydrate

The title complex, $[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, is a centrosymmetric oxalate-bridged binuclear Cu^{II} complex with an inversion center located at the mid-point of the C—C bond of the bridging oxalate ligand. The Cu atom has five-coordinate square-pyramidal geometry. A network of O—H...O hydrogen bonds helps to consolidate the crystal packing.

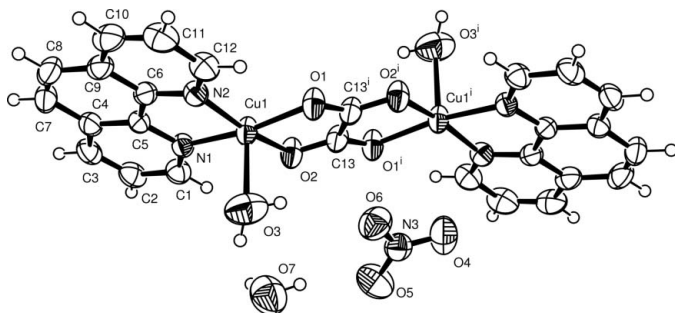
Comment

The oxalate (ox) group as a bidentate ligand plays an important role in polynuclear complexes (Cheng *et al.*, 2001), and many binuclear copper complexes with oxalate as the bridging ligand, such as $[\text{Cu}_2(\text{ox})(\text{dpq})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (dpq = dipyridoquinoxaline; Thomas *et al.*, 2002), $\text{Cu}_2(\text{phen})_2(\text{ox})(\text{NO}_3)_2$ (Bencini *et al.*, 1987) and $[\text{Cu}_2(\text{bpy})_2(\text{H}_2\text{O})_2(\text{ox})][\text{Cu}(\text{bpy})(\text{ox})](\text{NO}_3)_2$ (Julve *et al.*, 1984), have been crystallographically characterized. We report here the crystal structure of another binuclear copper complex with oxalate as bridging ligand that arises from a C—C bond fission (He *et al.*, 2004) of the gluconate ion under hydrothermal reaction conditions.



As shown in Fig. 1, the title complex, (I), is made up of a $[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation, two nitrate anions and two water molecules. The dication has an inversion center at the midpoint of the C—C bond of the bridging oxalate. In the dication, the Cu^{2+} environment is that of a distorted square pyramid composed of two phen N atoms and two O atoms of bridging oxalates at the corners of the basal square, and a fifth weakly coordinated water molecule at the apical position. The binding is somewhat different from that in $\text{Cu}_2(\text{phen})_2(\text{ox})(\text{NO}_3)_2$, where the Cu has the same basal square as (I) but the apical position is occupied by an NO_3^- anion (Bencini *et al.*, 1987). The Cu—N [1.9784 (16) and 1.9913 (16) Å] and Cu—O(ox) [1.9720 (14) and 1.9739 (14) Å] bonds as well as the Cu...Cu distance [5.135 (3) Å] are in good agreement with those [Cu—N = 1.991 (2) and 2.006 (2) Å; Cu—O(ox) = 1.987 (2) and 1.980 (2) Å; Cu...Cu = 5.158 (3) Å] in

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Figure 1

The structure of (I), showing the atom-labeling scheme, with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

[Cu₂(phen)₂(ox)(NO₃)₂]; however, only the Cu—O(water) bond [2.285 (2) Å] is slightly longer than the reported Cu—O(NO₃) bond [2.216 (2) Å].

Details of the hydrogen-bonding geometry and crystal packing of (I) are listed in Table 2. The O—H···O hydrogen-bond interactions (Fig. 2) stabilize the crystal structure of (I).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China without further purification. Addition of sodium gluconate (0.2181 g, 1 mmol) to an aqueous solution (30 ml) of Cu(NO₃)₂·3H₂O (0.4822 g, 2 mmol) gave a solution with a pH of 3.5. 1,10-Phenanthroline (0.3964 g, 2 mmol) was slowly added to the above solution with continuous stirring and the final pH was 4.0. The mixture was adjusted to pH 5.0 with a dilute solution of KOH and was hydrothermally treated at 383 K for 24 h. Blue block-shaped single crystals were isolated from the cool solution after several days.

Crystal data

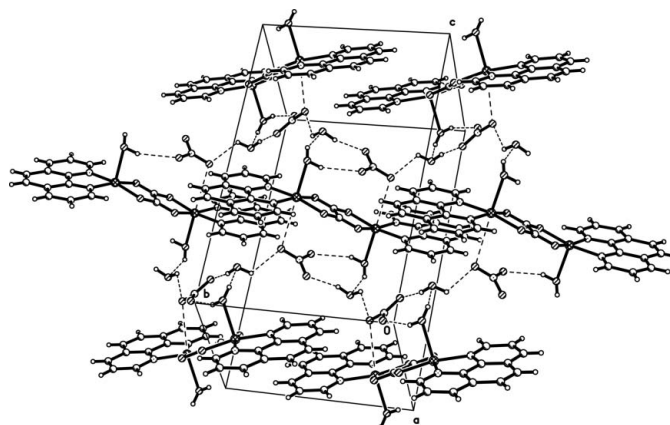
[Cu ₂ (C ₂ O ₄)(C ₁₂ H ₈ N ₂) ₂ (H ₂ O) ₂](NO ₃) ₂ ·2H ₂ O	$D_x = 1.751 \text{ Mg m}^{-3}$
$M_r = 771.59$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4718 reflections
$a = 7.7792$ (7) Å	$\theta = 2.2\text{--}26.0^\circ$
$b = 11.2380$ (11) Å	$\mu = 1.54 \text{ mm}^{-1}$
$c = 17.5795$ (15) Å	$T = 298$ (2) K
$\beta = 107.761$ (4)°	Block, blue
$V = 1463.6$ (2) Å ³	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	2862 independent reflections
φ and ω scans	2590 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$R_{\text{int}} = 0.013$
$T_{\text{min}} = 0.657, T_{\text{max}} = 0.750$	$\theta_{\text{max}} = 26.0^\circ$
7716 measured reflections	$h = -9 \rightarrow 9$
	$k = -12 \rightarrow 13$
	$l = -15 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.4467P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
2862 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
217 parameters	
H-atom parameters constrained	


Figure 2

The packing of (I). Dashed lines indicate hydrogen bonds.

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.9720 (14)	Cu1—N1	1.9913 (16)
Cu1—O2 ⁱ	1.9739 (14)	Cu1—O3	2.285 (2)
Cu1—N2	1.9784 (16)		
O1—Cu1—O2 ⁱ	85.19 (6)	N2—Cu1—N1	83.27 (7)
O1—Cu1—N2	169.04 (7)	O1—Cu1—O3	94.09 (8)
O2 ⁱ —Cu1—N2	92.32 (6)	O2 ⁱ —Cu1—O3	99.65 (8)
O1—Cu1—N1	96.83 (6)	N2—Cu1—O3	96.86 (8)
O2 ⁱ —Cu1—N1	167.02 (7)	N1—Cu1—O3	93.01 (8)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O3—H31···O1	0.86	2.62	3.122 (3)	118
O3—H32···O7	0.85	2.02	2.740 (3)	143
O7—H71···O6 ⁱⁱ	0.87	2.38	2.920 (3)	121
O7—H72···O5	0.86	2.03	2.873 (3)	168

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

H atoms attached to C atoms of (I) were placed in geometrically idealized positions, with $C_{\text{sp}^2}\text{—}H = 0.93$ Å, constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. H atoms attached to O atoms (water) of (I) were located in difference Fourier maps and refined as riding in their as-found relative positions, with $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$.

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) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL/PC.

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