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μ-Acetato-μ-aqua-μ-hydroxido-bis[(1,10-phenanthroline)copper(II)] dinitrate monohydrate

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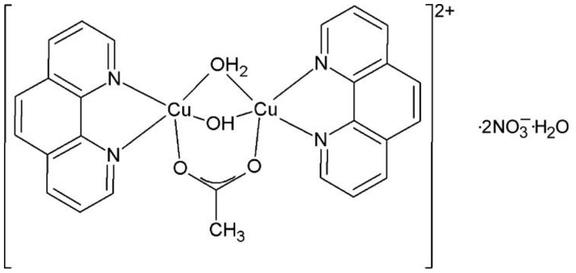
The triply bridged title dinuclear copper(II) compound, $[Cu_2(C_2H_3O_2)(OH)(C_{12}H_8N_2)_2(H_2O)](NO_3)_2\cdot H_2O$, (I), consists of a $[Cu_2(\mu_2\text{-}CH_3COO)(\mu_2\text{-}OH)(phen)_2(\mu_2\text{-}OH_2)]^{2+}$ cation (phen is 1,10-phenanthroline), two uncoordinated nitrate anions and one water molecule. The title cation contains a distorted square-pyramidal arrangement around each metal centre with a CuN_2O_3 chromophore. In the dinuclear unit, both Cu^{II} ions are linked through a hydroxide bridge and a triatomic bridging carboxylate group, and at the axial positions through a water molecule. The phenanthroline groups in neighbouring dinuclear units interdigitate along the [010] direction, generating several π–π contacts which give rise to planar arrays parallel to (001). These are in turn connected by hydrogen bonds involving the aqua and hydroxide groups as donors with the nitrate anions as acceptors. Comparisons are made with isostructural compounds having similar cationic units but different counter-ions; the role of hydrogen bonding in the overall three-dimensional structure and its ultimate effect on the cell dimensions are discussed.

Comment

Since the seminal work on copper acetate monohydrate reported by Bleaney & Bowers (1952), interest in magnetic dimeric (or dinuclear) compounds has been maintained for the past 60 years from different perspectives. This work has contributed to the field of molecular magnetic materials (Kahn, 1993) and to the understanding of correlations between exchange couplings and bond structure, and has helped in the design of new polynuclear molecular magnets. The fact that weakly interacting AFM (antiferromagnetic) dimeric magnetic materials display Bose–Einstein condensation at relatively high temperature (T) triggered considerable research by the materials and physics communities (Giamarchi *et al.*, 2008). The discovery of high-T_c superconductors also stimulated interest in interacting quantum spin systems, providing information about elementary excitations, quantum phase transitions and critical phenomena. Many studies of dimeric materials have been reported in this context. Our interest in dimeric materials is directed towards the effects of weak interactions between molecular units (Napolitano *et al.*, 2008; Perec *et al.*, 2010). Since the stacking of phenanthroline rings is a potential source of weak intermolecular exchange couplings, we have been looking for new compounds where dinuclear units are coupled by this type of interaction. During our studies, the triply bridged dinuclear copper(II) title compound, μ-acetato-μ-aqua-μ-hydroxido-bis[(1,10-phenanthroline)copper(II)] dinitrate monohydrate, (I), was obtained (Figs. 1–3).



(I)

The asymmetric unit of (I) consists of a $[Cu_2(\mu_2\text{-}CH_3COO)(\mu_2\text{-}OH)(phen)_2(\mu_2\text{-}OH_2)]^{2+}$ dinuclear cation (phen is 1,10-phenanthroline), two uncoordinated nitrate anions and one solvent water molecule (Fig. 1). The cation has a distorted square-pyramidal arrangement at each Cu^{II} ion, in such a way that the two pyramidal CuN_2O_3 chromophores share one edge. Both Cu^{II} ions are linked [Cu1$\cdots$Cu2 = 2.9559 (5) Å] at two equatorial positions through a hydroxide bridge [Cu—O =

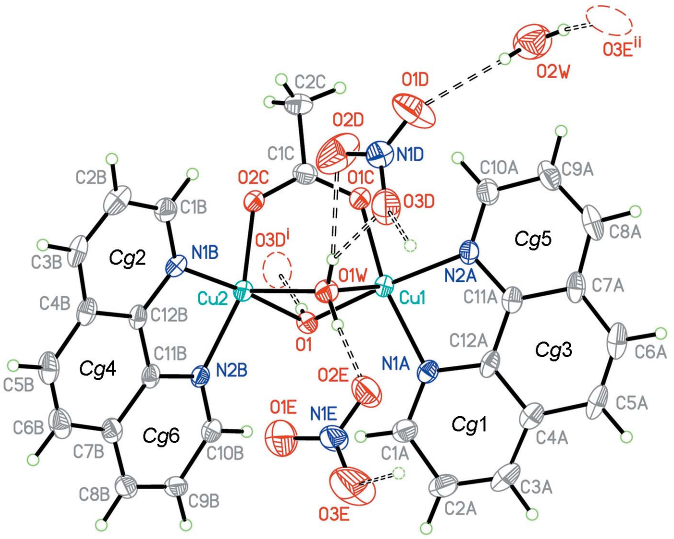


Figure 1
A molecular view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and hydrogen bonds are shown as double dashed lines. [Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$.]

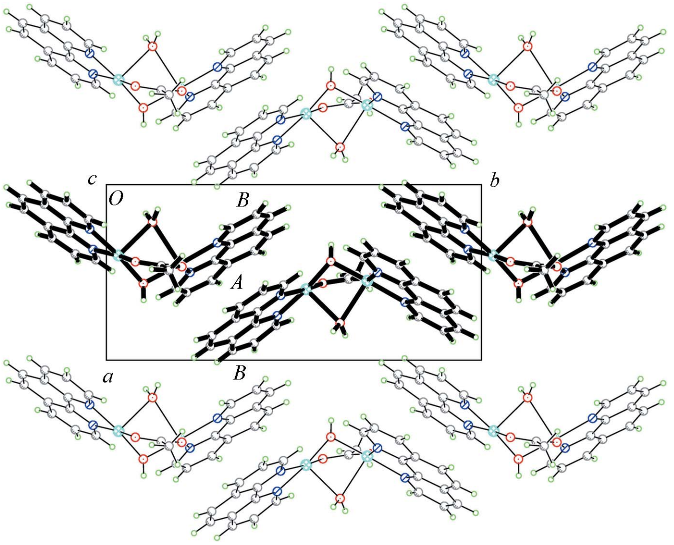


Figure 2
A packing diagram for (I), viewed along [001], showing how the dinuclear units are linked by π–π interactions into planes parallel to (001).

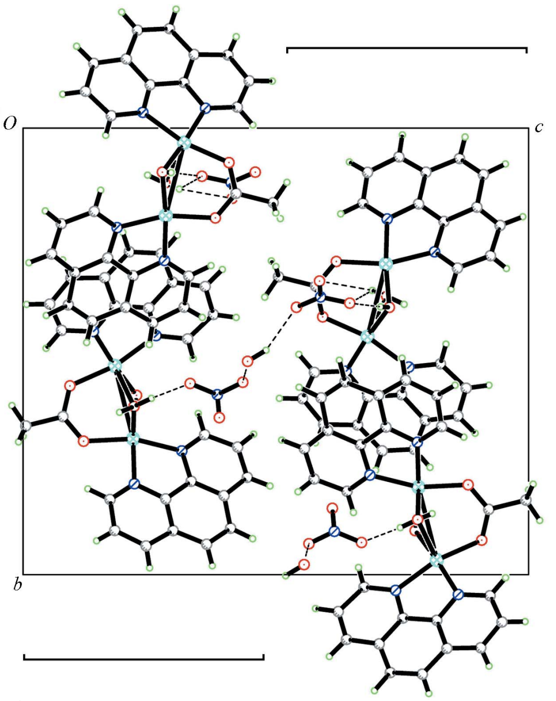


Figure 3
A packing diagram for (I), viewed along [100] and rotated by 90° compared with the view in Fig. 2, showing the hydrogen-bonding interactions (dashed lines). The (001) sheets are shown in projection as vertical structures (marked by square brackets).

1.928 (2) and 1.919 (2) Å for atoms Cu1 and Cu2, respectively] and a triatomic carboxylate bridge [Cu—O = 1.935 (2) and 1.940 (2) Å for atoms Cu1 and Cu2, respectively], and at the axial position through a water molecule [Cu—O = 2.344 (2) and 2.332 (2) Å for atoms Cu1 and Cu2, respectively]. The coordination of each Cu^{II} centre is completed by an *N*,*N*′-chelating phen ligand [Cu—N = 2.007 (3) and 2.023 (2) Å for Cu1, and 1.994 (3) and 2.016 (2) Å for Cu2]; the resulting bond valencies for the two cations are 2.16 and 2.20, respectively (*PLATON*; Spek, 2009). The polyhedron around Cu1 is slightly more regular than that about Cu2, displaying clear differences in the (ideally equal) *trans* O—Cu—N basal angles [6.56 (16) *versus* 16.48 (18)°, respectively], the deviation from planarity in the basal plane [0.032 (2) Å for N2*A* *versus* 0.205 (2) Å for N1*B*], the departure of the apical axis from the vertical [8.22 (12) *versus* 20.4 (2)°] and (perhaps as a summary) their τ parameters [as defined by Addison *et al.* (1984) and calculated using *PLATON*; 0.11 *versus* 0.27].

The ligands are featureless: neither of the phen groups departs significantly from planarity [maximum deviations = 0.028 (3) Å for C2*A* and 0.037 (3) Å for C11*B*] and the C—O bonds in the acetate group display an almost perfect resonance [O1*C*$\overset{\cdots}{-}$C1*C* = 1.249 (4) Å and O2*C*$\overset{\cdots}{-}$C1*C* = 1.252 (4) Å].

{Cu$_2$(OH)(H$_2$O)(carboxylate)} is a well known cluster and a search of the Cambridge Structural Database (CSD, Version 5.32 of 2011; Allen, 2002) revealed several structures incorporating the moiety [*e.g.* CSD refcodes CITLOH, CITLEX and YAFZUA01 (Youngme *et al.*, 2008); YEMNIO and YEMNEK (Chailuecha *et al.*, 2006); DIXGEX (Chen *et al.*, 2008); JEJCIK (Christou *et al.*, 1990); OLOVOA (Chadjistamatis *et al.*, 2003); QAHDUY (Sgarabotto *et al.*, 1999); YINJEL (Chen *et al.*, 2007), to mention just a few]. A comparative analysis within this set shows coordination distances over modest ranges (Cu—O$_{\rm hydroxy}$ = 1.908–1.933 Å, Cu—O$_{\rm carboxylate}$ = 1.925–1.993 Å and Cu—O$_{\rm water}$ = 2.321–2.415 Å), the values found for (I) being within these ranges. On the other hand, the intercationic distance for (I) appears distinctly shorter [Cu⋯Cu = 2.990–3.124 Å in the CSD *versus* Cu1⋯Cu2 = 2.9559 (5) Å in (I)].

A view of the {Cu$_2$(OH)(H$_2$O)(carboxylate)} clusters is provided in Fig. 4, presented as overlapping {Cu$_2$(OH)(H$_2$O)-(carboxylate)} clusters where only the Cu–(OH)–Cu bridge has been fitted, the remaining atoms having been omitted for clarity. It is obvious that a very reasonable match is observed for the carboxylates, while a much larger spread is observed

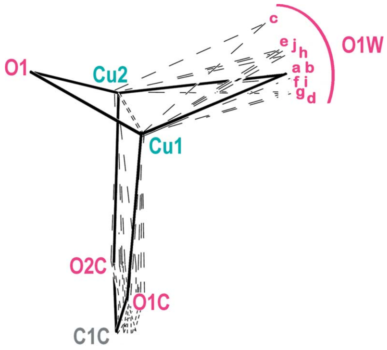


Figure 4
Comparison of the {Cu$_2$(OH)(H$_2$O)(carboxylate)} cluster in (I) (heavy lines) with examples from the literature. Structure codes a–j correspond to the following CSD refcodes and references: a = CITLOH, c = CITLEX and i = YAFZUA01 (Youngme *et al.*, 2008); b = YEMNIO and h = YEMNEK (Chailuecha *et al.*, 2006); d = DIXGEX (Chen *et al.*, 2008); e = JEJCIK (Christou *et al.*, 1990); f = OLOVOA (Chadjistamatis *et al.*, 2003); g = QAHDUY (Sgarabotto *et al.*, 1999); j = YINJEL (Chen *et al.*, 2007).

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for the aqua bridge. This may have to do with the weaker binding of the O_{water} atom to the cations, as well as the hydrogen-bonding ability of water. This makes it prone to disrupting interactions and modifying the ideal geometry.

Regarding the packing arrangement, the way in which the dinuclear units aggregate into a three-dimensional supramolecular structure can be described (for clarity) as a two-step process. The first step is achieved *via* the stacking of interwoven dinuclear units to form two-dimensional structures parallel to (001) (Fig. 2). The forces involved are several π–π interactions between the stacked phenanthroline groups, summarized in Table 2. These interactions are not evenly distributed. Firstly, there are zones with additional stronger bonds (labelled '*A*' in Fig. 2, entries 1–3 in Table 2) defining chains which run along the *b*-axis direction, and these chains are in turn connected by weaker/fewer links (zones labelled '*B*' in Fig. 2, entries 4–5 in Table 2) to form a broad two-dimensional structure. Secondly, a number of hydrogen bonds are present involving the NO_3^- counter-ions as acceptors and the hydroxy/aqua (Table 1, entries 1–6) and the outermost phen C—H groups (Table 1, entries 7–9) as donors. Fig. 3 shows a packing view rotated by 90° compared with that presented in Fig. 2, where the planar arrays are seen in projection, and the hydrogen-bonding network can be clearly observed. It is apparent that the cohesion provided by these interactions is partly intraplanar (providing for the plane stability) and partly interplanar, assisting the plane-to-plane linkage.

More detailed comparisons can be made of the three-dimensional structure in (I) with two isostructural analogues (mentioned earlier) which have the same phen ligand but different counter-anions (*L*), *viz.* *L* = BF_4^-, (II) (CITLOH; Youngme *et al.*, 2008), and *L* = ClO_4^-, (III) (YEMNIO; Chailuecha *et al.*, 2006). Both structures share the same dinuclear unit as (I) [mean square deviations of the fit of all non-H atoms = 0.075 (2) and 0.116 (2) Å, respectively] and are also interwoven in analogous π-bonded layers, but differ in the remaining interactions aggregating the components into a three-dimensional structure. It is relevant to stress for the following discussion that this hydrogen-bonding system appears stronger and more clearly defined in (I) than in either of the analogues (II) and (III), since the O-atom acceptors in the NO_3^- counter-ion of (I) are fairly well defined, while those in the BF_4^- and ClO_4^- analogues, (II) and (III), appear heavily disordered.

Comparison of the cell dimensions for all three structures (Table 3) yields information regarding the interactions governing the crystal packing and the way they operate [numbers in parentheses give the percentage differences from (I)]. It can be seen that, along the *c* axis, there are negligible differences between the three structures, while significant differences are noted along *a* and *b*. This fact correlates with the disposition and structure of the packing 'leitmotiv' shown in Fig. 2. The *c* direction is, in principle, defined by the width of the planes and this is basically associated with the volume occupied by the dinuclear unit; counter-ions are lodged in the intermolecular voids and, even though they provide interplanar cohesion, they do not appear to affect the mean planar width. Thus, the '*c*'-axis length would be limited by the 'bumping' of basically uncompressible planes. The remaining two directions, on the other hand, are contained in the plane, and along them the structure shows no significant cohesion forces able to oppose the strain introduced by any additional forces, *e.g.* hydrogen bonding. Thus, structure (I), with stronger and better defined intraplanar hydrogen-bonding interactions than (II) and (III) (see above), presents a detectable shrinkage of the planes in both the *a* and *b* directions, a fact directly ascribable to the internal hydrogen-bonding network and the flexibility of the π–π interactions to adapt to them. It is worth noting the highly hydrophilic character of both NO_3^- anions, in particular nitrate *D*, where atom O3*D*, for instance, accepts four hydrogen bonds of different type and strength.

Our structural results show promise in the search for new dinuclear materials with weak interactions between moieties. However, we have not yet overcome the problem of the specimens being too small for EPR (electron paramagnetic resonance) measurements, and are at present devoting our efforts to the growth of single crystals of adequate size and quality for this purpose.

Experimental

All chemicals were purchased from Sigma and were used as received. A solution of sodium acetate, $NaCH_3COO$ (4 m*M*, 0.328 g), in water (40 ml) was prepared and its pH adjusted to 3.5–4 with a 10% solution of HNO_3. Under continuous agitation, equimolar quantities of 1,10-phenanthroline and copper nitrate were added to this solution. After complete dissolution, the pH was adjusted to 4.5–5 with a 1 *N* solution of NaOH and 10% HNO_3, and the solution was then filtered and left to evaporate at room temperature. Small crystals of (I) suitable for X-ray diffraction were obtained after approximately three weeks.

Crystal data

$[Cu_2(C_2H_3O_2)(OH)(C_{12}H_8N_2)_2(H_2O)](NO_3)_2\cdot H_2O$
$M_r = 723.59$
Orthorhombic, $P2_12_12_1$
$a = 8.15051\ (15)$ Å
$b = 17.4091\ (3)$ Å
$c = 19.7447\ (4)$ Å
$V = 2801.63\ (9)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.59$ mm^{-1}
$T = 292$ K
0.35 × 0.20 × 0.15 mm

Data collection

Oxford Gemini CCD S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{min} = 0.54$, $T_{max} = 0.73$
16045 measured reflections
5135 independent reflections
3791 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.054$
$S = 0.91$
5135 reflections
422 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Absolute structure: Flack (1983), with 1687 Friedel pairs
Flack parameter: 0.001 (9)

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Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3*D*$^{\mathrm{i}}$	0.83 (3)	2.28 (3)	3.107 (4)	174 (3)
O1*W*—H1*WA*···O2*D*	0.84 (4)	2.21 (3)	2.943 (5)	145 (3)
O1*W*—H1*WA*···O3*D*	0.84 (4)	2.22 (3)	2.994 (5)	153 (3)
O1*W*—H1*WB*···O2*E*	0.84 (4)	1.91 (3)	2.745 (4)	171 (3)
O2*W*—H2*WA*···O1*D*	0.87 (4)	2.05 (3)	2.881 (6)	161 (6)
O2*W*—H2*WB*···O3*E*$^{\mathrm{ii}}$	0.87 (4)	1.99 (2)	2.835 (6)	164 (7)
C5*A*—H5*A*···O3*D*$^{\mathrm{iii}}$	0.93	2.52	3.408 (5)	160
C5*B*—H5*B*···O3*D*$^{\mathrm{iv}}$	0.93	2.52	3.402 (5)	158
C6*B*—H6*B*···O3*E*$^{\mathrm{v}}$	0.93	2.51	3.359 (6)	152

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

Table 2
π–π contacts (Å, °) for (I).

Centroid codes are as defined in Fig. 1. c.c.d. is the centroid–centroid distance, d.a. is the dihedral angle between rings and p.c.d. is the (mean) perpendicular distance from the centroid to the opposite plane (for details, see Janiak 2000).

Group 1/group 2	c.c.d. (Å)	d.a. (°)	p.c.d. (Å)
$Cg1\cdots Cg2^{\mathrm{i}}$	3.533 (2)	1.87 (17)	3.37 (2)
$Cg5\cdots Cg6^{\mathrm{i}}$	3.614 (2)	2.29 (17)	3.35 (3)
$Cg1\cdots Cg4^{\mathrm{i}}$	4.093 (2)	3.06 (17)	3.37 (4)
$Cg2\cdots Cg3^{\mathrm{ii}}$	3.628 (2)	1.32 (17)	3.35 (2)
$Cg3\cdots Cg6^{\mathrm{i}}$	3.578 (2)	1.68 (17)	3.39 (2)
$Cg4\cdots Cg5^{\mathrm{iii}}$	4.070 (2)	3.16 (17)	3.33 (2)

Symmetry codes: (i) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 3
Comparison of the unit-cell parameters for (I), (II) and (III).

Percentage values refer to differences from compound (I) reported herein.

Compound	*a* (Å)	*b* (Å)	*c* (Å)
(I)^{a}	8.1505 (2)	17.4091 (3)	19.7447 (4)
(II)^{b}	8.3452 (2) (2.38%)	17.7730 (2) (2.21%)	19.8477 (2) (0.52%)
(III)^{c}	8.3526 (5) (2.48%)	17.8236 (12) (2.38%)	19.9074 (13) (0.82%)

References: (*a*) this work; (*b*) Youngme *et al.* (2008); (*c*) Chailuecha *et al.* (2006).

Even though the geometry of the counter-ions allowed the groups to be initially interpreted as either acetate or nitrate, the final bond lengths and the lack of methyl H atoms in the difference maps confirmed nitrate as the correct assignment. All H atoms could be found in a difference Fourier map. Those attached to C atoms were placed in calculated positions, with phen C—H = 0.93 Å and methyl C—H = 0.96 Å, and allowed to ride. Those attached to O atoms were further refined with restrained O—H distances of 0.85 (1) Å and H···H distances of 1.35 (1) Å. The isotropic displacement parameter of the hydroxy H atom was refined. In all other cases, displacement parameters were taken as $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C,O})$ for methyl groups and water molecules, and as $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ otherwise.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3255). Services for accessing these data are described at the back of the journal.

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