metal-organic compounds

[{Cu(phen)₂}(μ-malato){Cu(phen)-(NO₃)}](NO₃)·4H₂O: malate acting as a tetradentate and dibridging ligand in a dinuclear copper complex

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The crystal structure of the title compound, μ-2-hydroxy-butanedioato-$1\kappa^2O^4,O^{4'}:2\kappa^3O^1,O^2,O^4$-nitrato-$2\kappa O$-tris(1,10-phenanthroline)-$1\kappa^4N,N';2\kappa^2N,N'$-dicopper(II) nitrate tetrahydrate, $[Cu_2(C_4H_3O_5)(NO_3)(C_{12}H_8N_2)_3](NO_3)\cdot4H_2O$, contains an unsymmetrical dinuclear copper complex with $Cu(phen)_2$ and $Cu(phen)(NO_3)$ moieties (phen is 1,10-phenanthroline) bridged by a malate (2-hydroxybutanedioate) ligand, which acts as a double-bridging and tetradentate ligand. As a result of this double-bridging action, especially the direct coordination of the O atom of one carboxylate group of malate to the two Cu atoms, the Cu···Cu distance is only 4.199 (1) Å and the two phen planes are roughly parallel [the shortest interplanar distance is 3.28 (1) Å], exhibiting an obvious intramolecular π–π stacking interaction.

Comment

Malic acid (H_2mal) has been found to be a versatile ligand in coordination compounds as it can exhibit many modes of coordination due to the presence of two carboxyl groups and one hydroxyl group. In some mononuclear complexes, e.g. $Na_3[WO_2H(S-mal)_2]$ [S-mal is (S)-malonate; Zhou et al., 2001] and $M_3[MoO_2H(S-mal)_2]\cdot H_2O$ (M is K or Na; Zhou et al., 2002), as well as in binuclear complexes such as $K_2[VO(O_2)-(Hmal)]_2\cdot2H_2O$ (Justino et al., 2003) and $Cs_2[\{VO_2(mal)\}_2]\cdot2H_2O$ (Biagioli et al., 2000), the malate anion acts as a bidentate ligand, coordinating to the metal through two O atoms from the hydroxyl group and the adjacent carboxylate group. In some binuclear complexes, such as $[Mn_2(Hmal)-(H_2O)_2]_2\cdot2H_2O$ (Liu et al., 2004), $[Zn(Hmal)(1,10-phen)-(H_2O)]_n$, $[Cu(Hmal)(2,2'-bipy)]_n\cdot3nH_2O$ (He et al., 2004) or $(NH_4)_2[VO(O_2)(Hmal)]_2\cdot2H_2O$ (Djordjevic et al., 1995), the malate anion is a tridentate ligand, coordinating to the metal ion through the hydroxyl O atom and two terminal

carboxylate O atoms. In the trinuclear complex $\{[Cu^I/Cu^{II}_2-(mal)(SO_4)(bpy)_2]\cdot H_2O\}_n$ (Lah et al., 2003), the malate anion connects the two crystallographically independent Cu^{II} ions by monodentate coordination of the two terminal carboxylate groups and through the hydroxyl O atom, which serves as a bridge between the two metal centres. We report here the crystal structure of (I), in which the malate ligand acts as a double bridging and tetradentate agent.


(I)
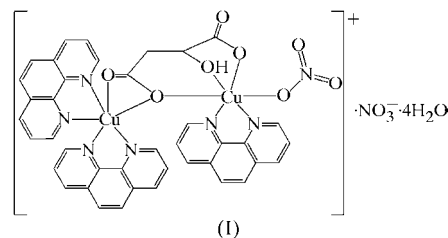
Some features of the molecular geometry of (I) are listed in Table 1 and the molecular conformation is illustrated in Fig. 1. The asymmetric unit of (I) consists of a $[Cu_2(mal)(NO_3)-(phen)_3]$ cation, a nitrate anion and four water molecules. In the cation, the coordination geometries around atoms Cu1 and Cu2 can be described as distorted octahedra with obvious Jahn–Teller distortion. Atom Cu1 is coordinated by four N atoms from two phen ligands and two O atoms from the same carboxylate group of the malate ligand, with atoms N1, N2, N3 and O4 in equatorial positions and atoms N4 and O5 at the Jahn–Teller axis. Atom Cu2 is coordinated by two N atoms from the third phen ligand and by four O atoms; the N atoms and the two O atoms from the hydroxyl group and the other carboxylate group of the malate form the equatorial plane, while the O atom of a nitrate and atom O4, shared with Cu1, occupy the Jahn–Teller axis. The two coordinated moieties are thus connected not only through the malate dianion as a bridge, but also through atom O4 of one carboxylate group of the malate ligand as another bridge directly coordinating to the two Cu^{2+} ions of the two moieties, forming an unsymmetric dinuclear copper complex. Therefore, the malate ligand plays the role of a double-bridging and tetradentate agent in this cation.

Bridging atom O4 links the two octahedra, with the Cu1—O4—Cu2 angle being 131.8 (1)°. As a result of this bridging action by atom O4, the two coordinated moieties are very close, with a Cu···Cu distance of 4.199 (1) Å. The two phen planes between the two moieties are roughly parallel, with a closest distance of 3.28 (1) Å, exhibiting an obvious intramolecular π–π stacking interaction.

Because of this double-bridging action, the structure of (I) obviously differs from that of the previously reported analogous complex $[Cu_2(IDA)(phen)_3](ClO_4)_2\cdot CH_3OH$ (IDA is iminodiacetate; Wei et al., 2004), where the similar $Cu(phen)_2$ and $Cu(phen)$ moieties are bridged by the IDA ligand, but the two O atoms of one carboxylate group of the IDA ligand are coordinated to the two Cu^{2+} ions, making these ions five-coordinated in a distorted trigonal–bipyramidal or square pyramidal environment, and no intramolecular π–π stacking interactions exist in this compound. Thus, the structure of the cation of (I) is unusual.
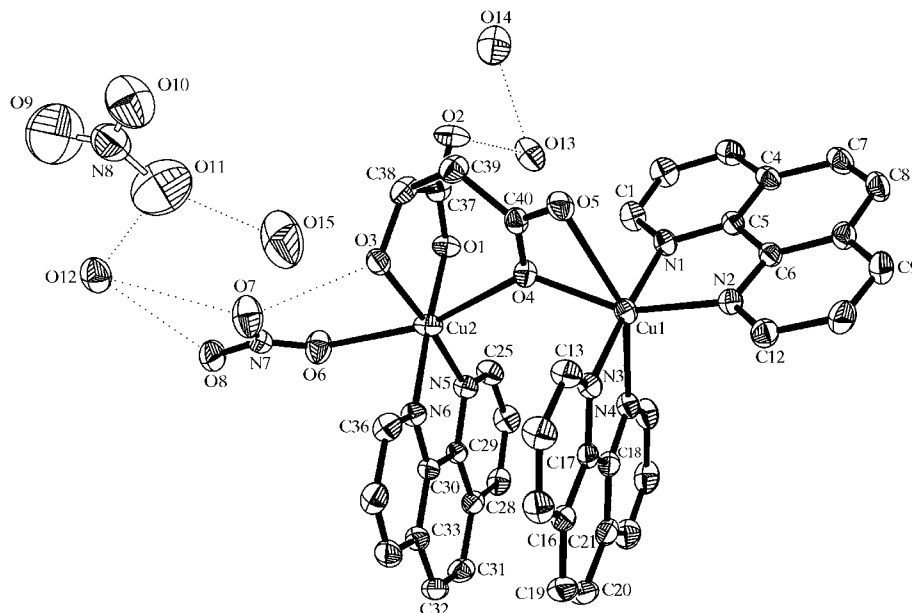
Figure 1
The structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 20% probability level. Hydrogen bonds are shown as dashed lines. The minor disorder components and H atoms have been omitted for clarity.
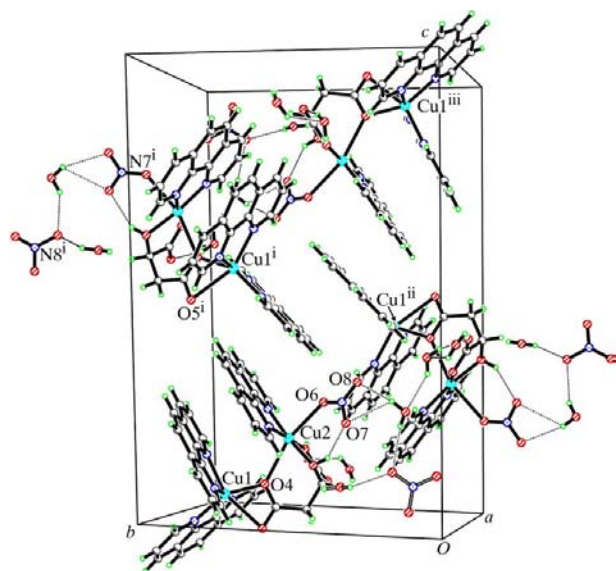
Figure 2
Hydrogen bonds (dashed lines) and π–π stacking interactions in (I). [Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $1 - x, 1 - y, 1 - z$.]

Details of the hydrogen-bonding geometry and crystal packing of (I) are listed in Table 2 and illustrated in Figs. 1 and 2. Only O—H$\cdots$O hydrogen bonds are observed in (I). In the crystal packing, four complex cations are stacked in each cell (Fig. 2) through intra- and intermolecular π–π stacking interactions via the partially overlapped phenanthroline rings, with centroid–centroid distances of 3.566 (3) (between N6/C30/C33–C36 and C16–C21), 3.634 (3) [between C4–C9 and C4^i–C9^i; symmetry code: (i) $-x + 1, -y + 2, -z$] and 3.762 (3) Å [between N2/C6/C9–C12 and C28^{ii}–C33^{ii}; symmetry code: (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$].

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company, China, and were used without further purification. Addition of malic acid (1 mmol) to an aqueous solution (10 ml) of $Cu(NO_3)_3 \cdot 3H_2O$ (1 mmol) gave a solution of pH 1.5. 1,10-Phenanthroline (1 mmol) was added slowly to this solution with continuously stirring. The mixture was then adjusted to pH 3.0 with a dilute solution of KOH and kept at room temperature. Several days later, blue block-shaped single crystals of (I) were isolated.

Crystal data

$[Cu_2(C_4H_3O_5)(NO_3)(C_{12}H_8N_2)_3]$- $(NO_3) \cdot 4H_2O$	Mo $K\alpha$ radiation
$M_r = 995.85$	Cell parameters from 3837 reflections
Monoclinic, $P2_1/c$	$\theta = 2.0–23.7°$
$a = 12.448 (3)$ Å	$\mu = 1.11$ mm^{-1}
$b = 14.878 (4)$ Å	$T = 298 (2)$ K
$c = 22.483 (6)$ Å	Block, blue
$\beta = 97.655 (5)°$	$0.15 \times 0.12 \times 0.10$ mm
$V = 4127.1 (19)$ Å^3	
$Z = 4$	
$D_x = 1.603$ Mg m^{-3}	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	4946 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.036$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$\theta_{max} = 25.0°$
$T_{min} = 0.851$, $T_{max} = 0.897$	$h = -14 \rightarrow 14$
20979 measured reflections	$k = -17 \rightarrow 13$
7256 independent reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} = 0.001$
7256 reflections	$\Delta\rho_{max} = 0.88$ e Å^{-3}
623 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.998 (3)	Cu2—O1	1.909 (3)
Cu1—N1	2.002 (3)	Cu2—O3	1.962 (3)
Cu1—O4	2.043 (3)	Cu2—N6	1.985 (3)
Cu1—N2	2.059 (3)	Cu2—N5	1.993 (3)
Cu1—N4	2.171 (3)	Cu2—O6	2.519 (3)
Cu1—O5	2.587 (3)	Cu2—O4	2.551 (3)
Cu1···Cu2	4.1993 (13)		
N3—Cu1—N1	176.73 (13)	O1—Cu2—N6	176.67 (13)
N3—Cu1—O4	93.35 (12)	O3—Cu2—N6	97.79 (13)
N1—Cu1—O4	89.90 (12)	O1—Cu2—N5	94.41 (12)
N3—Cu1—N2	95.57 (12)	O3—Cu2—N5	172.92 (13)
N1—Cu1—N2	81.33 (13)	N6—Cu2—N5	82.90 (13)
O4—Cu1—N2	152.72 (11)	O1—Cu2—O6	93.68 (12)
N3—Cu1—N4	79.86 (12)	O3—Cu2—O6	88.25 (12)
N1—Cu1—N4	99.89 (12)	N6—Cu2—O6	88.04 (13)
O4—Cu1—N4	101.64 (11)	N5—Cu2—O6	84.73 (12)
N2—Cu1—N4	105.28 (12)	O1—Cu2—O4	82.09 (10)
N3—Cu1—O5	89.86 (11)	O3—Cu2—O4	75.14 (10)
N1—Cu1—O5	91.66 (11)	N6—Cu2—O4	97.06 (11)
O4—Cu1—O5	55.18 (10)	N5—Cu2—O4	111.82 (11)
N2—Cu1—O5	99.06 (11)	O6—Cu2—O4	163.11 (10)
N4—Cu1—O5	154.32 (10)	Cu1—O4—Cu2	131.84 (12)
O1—Cu2—O3	85.12 (12)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O7	0.83	2.11	2.841 (5)	147
O12—H12A···O8	0.83	2.43	3.092 (5)	137
O12—H12A···O7	0.83	2.62	3.043 (6)	113
O12—H12B···O11A	0.83	2.29	2.936 (13)	136
O12—H12B···O11B	0.83	2.20	2.801 (13)	130
O13—H13A···O2	0.83	2.05	2.864 (5)	164
O13—H13B···O12^i	0.82	2.10	2.799 (5)	142
O14—H14A···O13	0.82	2.24	2.859 (6)	133
O14—H14B···O5^{ii}	0.82	2.03	2.810 (5)	157
O15A—H51A···O11A	0.83	2.23	2.578 (16)	105

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

H atoms attached to O atoms were located in difference Fourier maps and refined with a global U_{iso}(H) value. The O—H distances are in the range 0.768–0.835 Å. H atoms attached to C atoms were placed in geometrically idealized positions, with Csp^3—H = 0.97 Å and Csp^2—H = 0.93 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). Atoms O9, O10, O11 and O15 of the nitrate anion and solvent water molecules were found to be disordered and were modelled over two sets of positions using restraints on their anisotropic displacement parameters. The major and minor disorder components had refined occupancies of 64.9 (5) and 35.1 (5)%, respectively.

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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