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Bis[μ_3-*cis*-*N*-(2-aminopropyl)-*N*′-(2-carboxylatophenyl)oxamidato(3−)]-bis(2,2′-bipyridine)dichloridotetra-copper(II) dihydrate

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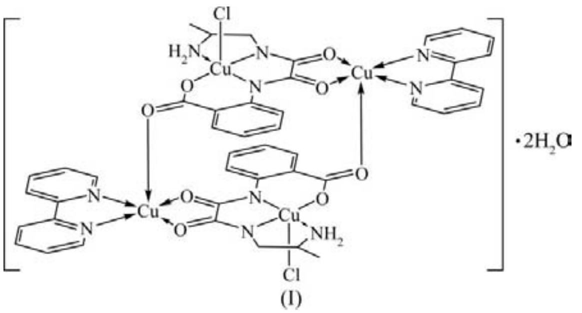
The title complex, bis[μ_3-*cis*-*N*-(2-aminopropyl)-*N*′-(2-carboxylatophenyl)oxamidato(3−)]-1:2:4κ^7*N*,*N*′,*N*″,*O*:*O*′,*O*″:*O*‴;-2:3:4κ^7*O*‴:*N*,*N*′,*N*″,*O*:*O*′,*O*″-bis(2,2′-bipyridine)-2κ^2*N*,*N*′;4κ^2*N*,*N*′-dichlorido-1κ*Cl*,3κ*Cl*-tetracopper(II) dihydrate, $[Cu_4(C_{12}H_{12}N_3O_4)_2Cl_2(C_{10}H_8N_2)_2]\cdot 2H_2O$, consists of a neutral cyclic tetracopper(II) system having an embedded centre of inversion and two solvent water molecules. The coordination of each Cu^{II} atom is square-pyramidal. The separations of Cu^{II} atoms bridged by *cis*-*N*-(2-aminopropyl)-*N*′-(2-carboxylatophenyl)oxamidate(3−) and carboxyl groups are 5.2096 (4) and 5.1961 (5) Å, respectively. A three-dimensional supramolecular structure involving hydrogen bonding and aromatic stacking is observed.

Comment

It is known that *N*,*N*′-bis(substituted)oxamides could be good candidates in forming polynuclear complexes because their coordinating ability toward transition metal ions can be modified and tuned by changing the nature of the amide substituents (Ojima & Nonoyama, 1988). A typical feature of these ligands is an easy transformation of *cis*–*trans* conformations, which makes it practical to design tunable molecular materials with desired properties (Ruiz *et al.*, 1999). To date, many polynuclear complexes containing oxamide bridges have been synthesized and their properties have been studied extensively (Messori *et al.*, 2003; Wang *et al.*, 2004). Compared with studies dealing with symmetrical *N*,*N*′-bis(substituted)oxamide polynuclear systems, relatively few studies dealing with dissymmetrical *N*,*N*′-bis(substituted)oxamide polynuclear complexes have been reported, owing to difficulties in their synthesis (Matović *et al.*, 2005; Zang *et al.*, 2003). However, the fact that those complexes bridged by dissymmetrical *N*,*N*′-bis(substituted)oxamides have shown predominant properties (Costes *et al.*, 2000; Erxleben, 2001; Larionova *et al.*, 1997; Pei *et al.*, 1989, 1991) stimulated us to design and synthesize new polynuclear complexes with dissymmetrical *N*,*N*′-bis(substituted)oxamides to explore their special structures and functionalities. In continuation of our earlier work (Li *et al.*, 2003, 2004; Liu *et al.*, 2008), we synthesized a novel tetranuclear copper(II) complex bridged by the asymmetrical oxamide ligand *cis*-*N*-(2-aminopropyl)-*N*′-(2-carboxylatophenyl)oxamidate(3−) ($oxbm^{3-}$) and end-capped with 2,2′-bipyridine (bpy), namely $[Cu_4(oxbm)_2Cl_2(bpy)_2]\cdot 2H_2O$, (I), and report the crystal structure here.



(I)

A perspective view of complex (I) is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 1. As shown in Fig. 1, the asymmetric unit can be considered as a *cis*-oxamide-bridged dinuclear copper(II) complex linked with a solvent water molecule by an O—H···Cl hydrogen bond, *viz.* $[Cu_2(oxbm)Cl(bpy)]\cdot H_2O$. Through carboxyl bridges, a pair of units assemble to form a circular tetranuclear system with inversion symmetry. The *cis*-oxamide group coordinates to

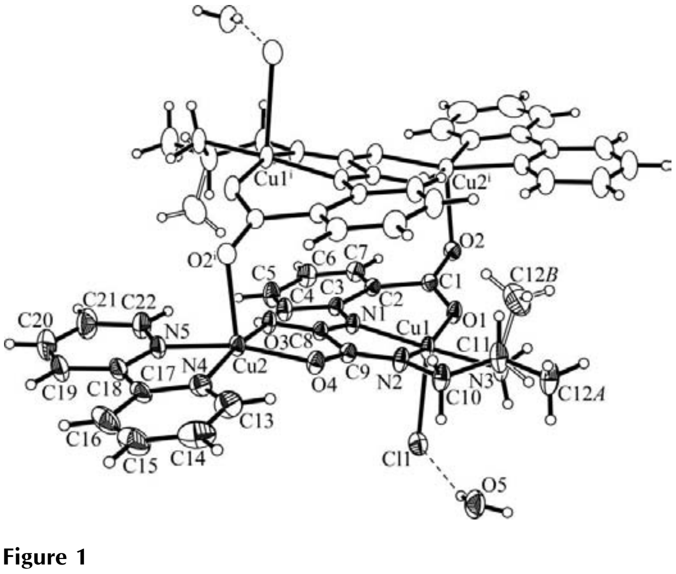


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For clarity, the atoms of the asymmetric residue unit and its counterpart are represented in different styles, and the bonds of C12*B* are depicted with open lines. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) −*x* + 1, −*y*, −*z* + 1.]

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atoms Cu1 and Cu2 in the usual chelating mode, with bite angles of 83.40 (9) and 85.23 (8)°, respectively. The carboxylate group bridges Cu atoms in a nonplanar skew–skew fashion. The Cu1—O1—C1—O2 and Cu2^{i}—O2—C1—O1 torsion angles [symmetry code: (i) $-x + 1, -y, -z + 1$; Table 1] are similar to those found in other complexes with skew–skew carboxyl bridges (Duan *et al.*, 2006; Tong *et al.*, 1997). The Cu···Cu separations through the oxamide and carboxylate bridges are 5.2096 (4) and 5.1961 (5) Å, respectively. To date, seven cyclic tetranuclear complexes with symmetrical oxamide bridges have been synthesized and structurally characterized (Abbati *et al.*, 1999; Li *et al.*, 2008; Ribas *et al.*, 1998; Zhu *et al.*, 2007). However, the title complex is the first instance of a dissymmetrical oxamide.

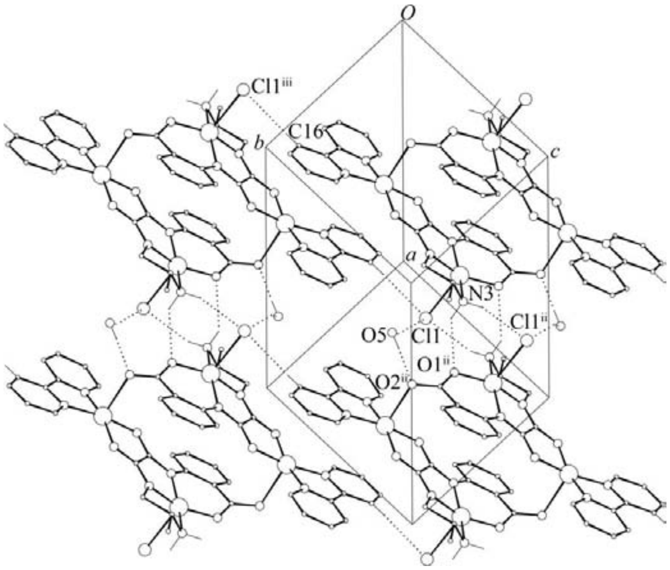

Figure 2
A view of the two-dimensional hydrogen-bonding structure of (I). Hydrogen bonds are shown as dotted lines and H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii) $-x + 2, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z$.]

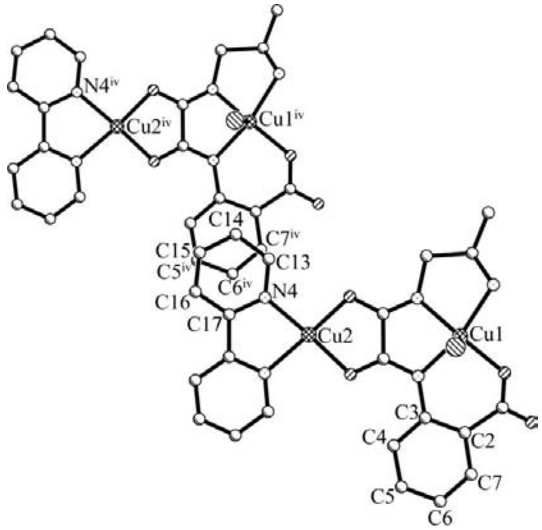

Figure 3
A view showing the π–π stacking interactions along the c axis, viewed perpendicular to the pyridine plane. H atoms and water molecules have been omitted for clarity. [Symmetry code: (iv) $x, y, z - 1$.]

Atoms Cu1 and Cu2 are both in square-pyramidal coordination geometries, with τ values of 0.08 and 0.03 (Addison *et al.*, 1984), respectively. Atom Cu1 resides in an inner site of the *cis*-oxbm^{3-} ligand; the basal plane is defined by atoms N1, N2, N3 and O1, and the maximum displacement from the least-squares plane is 0.1073 (15) Å for N2, the displacement of atom Cu1 being 0.2403 (13) Å. The apical position is occupied by atom Cl1. Atom Cu2 coordinates to the *exo-cis* O atoms of the oxbm^{3-} ligand (O3 and O4), and the N atoms (N4 and N5) of the bpy ligand complete the basal plane, from which the maximum deviation is 0.0190 (12) Å (N4). The apical site is occupied by a carboxyl O atom (O2^{i}). Atom Cu2 is pulled 0.2101 (12) Å out of the basal plane by the apical O2^{i} atom.

The oxbm^{3-} ligand chelates atom Cu1 to form two five-membered and one six-membered chelate ring. One of the five-membered rings is planar, and the other has an envelope conformation puckered on the chiral C11 atom, the puckering parameters (Cremer & Pople, 1975) being $Q = 0.399$ (3) Å and $\varphi = 114.2$ (4)°. The six-membered ring adopts a boat conformation, with puckering parameters $Q = 0.304$ (3) Å, $\theta = 87.9$ (6)° and $\varphi = 300.8$ (5)°. The Cu1—N1 and Cu1—N2 bonds are shorter than the Cu1—N3 bond (Table 1), which is consistent with the stronger donor ability of the deprotonated amide N atom compared with the primary amine N atom (Jubert *et al.*, 2002).

In the crystal structure, neutral tetranuclear complexes and solvent water molecules are connected by classical hydrogen bonds into a one-dimensional chain parallel to the a axis (Table 2). The chains are linked through nonclassical C—H···Cl hydrogen bonds into a two-dimensional hydrogen-bonding network extending along the (011) plane (Fig. 2). Moreover, offset π–π stacking is observed between the pyridine ring containing atom N4 and the benzene ring of a neighbouring complex, the nearest separation being 3.421 (4) Å for atom C6^{iv} [symmetry code: (iv) $x, y, z - 1$; Fig. 3]. The stackings dominate the interactions between the hydrogen-bonded layers and hold them together to create a three-dimensional supramolecular structure.

Experimental

All reagents were of analytical reagent grade and were used without further purification. A methanol (5 ml) solution of $CuCl_2·2H_2O$ (0.0085 g, 0.05 mmol) was added dropwise to an aqueous solution (5 ml) of Na[Cu(oxbm)] (0.0349 g, 0.1 mmol), prepared according to the method described by Tao *et al.* (2003), with continuous stirring. The mixture was stirred quickly for an hour and then a solution of 2,2′-bipyridine (0.0078 g, 0.05 mmol) in methanol (5 ml) was added dropwise. The resulting solution was stirred at 333 K for 6 h, filtered and the filtrate allowed to stand at room temperature for one week to give well shaped green crystals suitable for X-ray analysis (yield 72%). Elemental analysis calculated for $C_{44}H_{44}Cl_2Cu_4N_{10}O_{10}$: C 44.11, H 3.70, N 11.69%; found: C 44.31, H 3.78, N 11.71%.

Crystal data

$[Cu_4(C_{12}H_{12}N_3O_4)_2Cl_2(C_{10}H_8N_2)_2]\cdot 2H_2O$
$M_r = 1197.95$
Triclinic, $P\bar{1}$
$a = 10.9622\ (1)$ Å
$b = 11.1330\ (2)$ Å
$c = 11.2876\ (2)$ Å
$\alpha = 67.072\ (1)^\circ$
$\beta = 69.842\ (1)^\circ$
$\gamma = 72.688\ (1)^\circ$
$V = 1169.57\ (3)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 1.98$ mm^{-1}
$T = 298\ (2)$ K
0.28 × 0.22 × 0.17 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
$T_{\min} = 0.607$, $T_{\max} = 0.730$
16602 measured reflections
5441 independent reflections
4353 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.098$
$S = 1.04$
5441 reflections
328 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.98$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1	2.6832 (10)	Cu2—N4	1.961 (2)
Cu1—N1	1.988 (2)	Cu2—N5	2.000 (3)
Cu1—N2	1.925 (2)	Cu2—O2$^{\rm i}$	2.276 (2)
Cu1—N3	2.035 (2)	Cu2—O3	1.9586 (19)
Cu1—O1	1.9188 (19)	Cu2—O4	1.9430 (19)
N1—Cu1—N2	83.40 (9)	O3—Cu2—O4	85.23 (8)
Cu1—O1—C1—O2	155.8 (2)	Cu2$^{\rm i}$—O2—C1—O1	−103.9 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···Cl1	0.92	2.47	3.335 (3)	159
O5—H5B···O2$^{\rm ii}$	0.81	2.07	2.870 (3)	168
N3—H3B···Cl1$^{\rm ii}$	0.90	2.55	3.406 (2)	158
N3—H3A···O1$^{\rm ii}$	0.90	2.44	3.172 (3)	138
C16—H16···Cl1$^{\rm iii}$	0.93	2.70	3.549 (4)	152

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

The methyl group was disordered over two positions, C12*A* and C12*B*, whose occupancy factors were refined and then fixed at 0.7 and 0.3, respectively. The C11—C12*B* bond length was restrained to a reasonable C—C value [1.456 (7) Å], and similarity restraints with a standard uncertainty of 0.01 Å were applied to the C10···C12*A* and C10···C12*B* distances as well as to the N3···C12*A* and N3···C12*B* distances. Water H atoms were found in a difference Fourier map and were treated as riding, with fixed $U_{\rm iso}$(H) values of 0.08 Å^2. The remaining H atoms were placed in calculated positions, with N—H = 0.90 Å and C—H = 0.93 (aromatic), 0.96 (methyl), 0.97 (methylene) or 0.98 Å (methine), and refined in riding mode, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N) or $1.5U_{\rm eq}$(methyl C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*a*); molecular graphics: *XP* (Siemens, 1994) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3285). Services for accessing these data are described at the back of the journal.

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