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Aqua[3,6-bis(methoxycarbonylmethyl)-3,6-diazaoctanedioato]copper(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.033
wR factor = 0.072
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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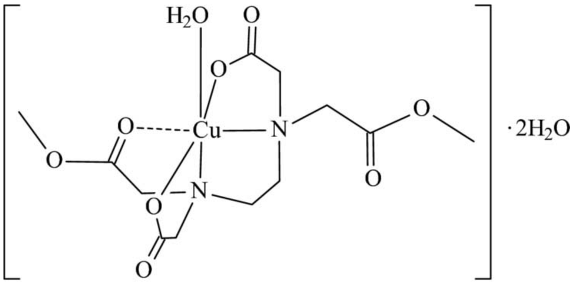
The title complex, $[Cu(C_{12}H_{18}N_2O_8)(H_2O)]\cdot 2H_2O$, crystallizes with the tetradentate ethylenediaminetetraacetic acid (edta) diester derivative and one water molecule forming a pyramidal environment. The vacant site of the octahedral complex is remotely associated with an O atom of one of the carbonyl atoms of the edta derivative.

Comment

In our quest for alternative immobilized metal affinity chromatography (IMAC) ligands (Porath *et al.*, 1975) that may be tethered to a solid support, ethylenediaminetetraacetic acid (edta) esters have been investigated. Esterifying two of the four acid groups of the potentially hexadentate edta ligand reduces it to a tetradentate ligand, providing two open sites in the octahedral coordination for selective coordination to the target compound (usually enzymes and proteins) to be purified by IMAC, and simultaneously using the ester group to anchor the ligand to the tether. The dimethyl ester of edta has been used as a model compound in order to investigate the coordination arrangement of the ligand, since the availability of adjacent sites is advantageous in IMAC.



(I)

The dimethyl ester of edta was prepared by refluxing edta dianhydride in an excess of methanol. The resultant ligand was complexed to basic copper(II) carbonate in water at 333 K, and allowed to crystallize, yielding the title complex, (I), with two molar equivalents of water in the asymmetric unit. The tetradentate ligand has the desired configuration (Fig. 1), coordinating through the two free carboxylates and both amine groups, with the two remaining sites of the Cu coordination adjacent. A coordinated water molecule and the carbonyl O atom of one of the ester groups complete the severely Jahn–Teller distorted octahedral configuration around the Cu atom; see Table 1. The axial Cu—O distance is nearly 0.6 Å longer than the two equatorial Cu—O(carboxylate) distances, while the axial Cu—N bond is 0.25 Å longer than its equatorial counterpart. Furthermore,

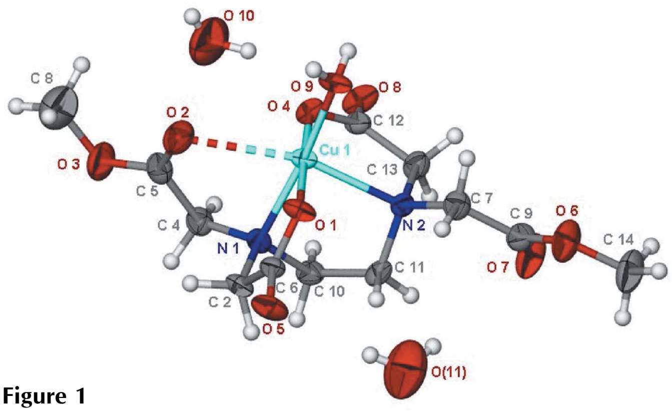


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

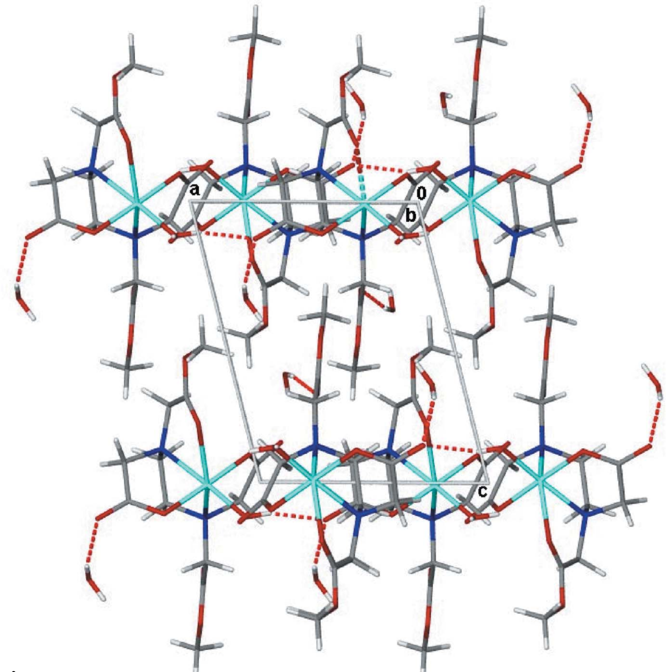


Figure 2
The packing of (I), showing the hydrogen-bonding (dashed lines) pattern of layers parallel to the *ab* plane.

the two axial ligands are bent away from the water ligand, such that the O2—Cu1—N2 angle is 154.03 (9)°.

The two five-membered N—O(carboxylate) chelate rings that coordinate through equatorial O atoms are both essentially planar, the largest deviations from planarity being 0.097 (2) Å for C13 and 0.098 (2) Å for C2. The five-membered N—O(ester carbonyl) chelate ring coordinating through the axial O is, on the other hand, twisted, with the largest deviation from planarity exhibited by N1 [0.305 (2) Å]. A further indication of the twisting can be seen in the Cu1—N1—C4—C5 torsion angle of −39.8 (3)°.

Each H atom of the coordinated water molecule participates in hydrogen bonding (see Table 2) with one of the coordinated carboxylate groups of two neighbouring complexes. This leads to the formation of layers of the complexes parallel to the *ab* plane (see Fig. 2). The terminal ester groups of the edta derivative and the free water molecules lie between these layers, with the two water molecules hydrogen bonded to the carbonyl O atoms of a bound carboxylate and a free ester group, respectively.

Experimental

Preparation of dimethyl *N*,*N*′-bis(carboxymethyl)-3,6-diazaoctanedioate (DMDDO): ethylenediaminetetraacetic dianhydride (5.00 g, 20 mmol) was mixed with methanol (100 ml) and refluxed for 6 h. The solution was filtered while hot and the methanol removed under reduced pressure. The residue was dissolved in refluxing ethyl acetate (50 ml) and allowed to crystallize below 273 K. The crystals were filtered off and washed with diethyl ether and dried under high vacuum, yielding dimethyl *N*,*N*′-bis(carboxymethyl)-3,6-diazaoctanedioate (yield 6.27 g, 98%). ν_{max} (cm^{-1}, KBr, Perkin–Elmer 1720 F T–IR spectrophotometer): 3474 (w), 3024 (*m*), 2996 (*w*), 2967 (*m*), 1750 (*vs*, ester carbonyl), 1632 (*s*, carboxylate carbonyl), 1471 (*sh*), 1444 (*s*), 1402 (*s*), 1241 (*vs*), 1216 (*s*) and 1087 (*m*); ^{1}H NMR ($CDCl_3$, Varian VXR 300, 300 MHz): δ 2.73 (*s*, 4H, $-NCH_2CH_2N-$), 3.43 (*s*, 4H, $-CH_2$-acid), 3.55 (*s*, 4H, $-CH_2$-ester) and 3.60 (*s*, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, Varian VXR 300, 75 MHz): δ 50.89 (*q*, $-CH_3$) 51.2 (*t*, $-NCH_2CH_2N-$), 54.1 (*t*, $-CH_2$-ester), 54.4 (*t*, $-CH_2$-acid), 171.2 (*s*, –COO-ester) and 172.2 (*s*, –COOH); *e*/*z* (EI): 320 (100%, M^+).

Preparation of (I): DMDDO (1.00 g, 3.1 mmol) was dissolved in distilled water (5 ml) at 333 K. $CuCO_3 \cdot Cu(OH)_2$ (238 mg, 1.6 mmol) was added with stirring until dissolved and the evolution of carbon dioxide ceased. Deep-blue crystals formed at ambient temperature. The crystals were filtered off and washed with ice-cold ethanol, yielding 1.05 g (89%) of (I). ν_{max} (cm^{-1}, KBr): 3443 (*s*, *br*), 2956 (*m*), 1739 (*vs*, ester carbonyl), 1610 (*vs*, carboxylate carbonyl), 1436 (*m*), 1381–2 (*s*), 1255 (*sh*), 1221–2 (*s*), 1117–8 (*s*); *e*/*z* (EI): 382 (M^+).

Crystal data

$[Cu(C_{12}H_{18}N_2O_8)(H_2O)]\cdot 2H_2O$
$M_r = 435.87$
Monoclinic, $P2_1$
$a = 7.5208\ (15)$ Å
$b = 13.158\ (3)$ Å
$c = 9.5684\ (19)$ Å
$\beta = 104.31\ (3)^\circ$
$V = 917.5\ (4)$ Å^3
$Z = 2$
$D_x = 1.578$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 1895 reflections
$\theta = 1.0$–27.5°
$\mu = 1.25$ mm^{-1}
$T = 173\ (2)$ K
Prism, deep-blue
0.37 × 0.25 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.70$, $T_{max} = 0.86$
4595 measured reflections
3207 independent reflections
2958 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0^\circ$
$h = -9 \rightarrow 8$
$k = -16 \rightarrow 14$
$l = -7 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.072$
$S = 1.04$
3207 reflections
259 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.0434P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983), 1318 Friedel pairs
Flack parameter: 0.019 (14)

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Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.918 (2)	Cu1—O9	1.956 (2)
Cu1—O2	2.545 (3)	Cu1—N1	2.080 (3)
Cu1—O4	1.951 (2)	Cu1—N2	2.326 (3)
O1—Cu1—O4	176.58 (11)	O9—Cu1—N1	170.86 (12)
O2—Cu1—O9	101.32 (10)	O9—Cu1—N2	102.95 (10)
O2—Cu1—N2	154.03 (9)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H102···O7^{i}	0.81 (4)	2.23 (3)	3.024 (5)	167 (6)
O9—H92···O8^{i}	0.844 (18)	1.851 (19)	2.695 (4)	178 (4)
O9—H91···O5^{ii}	0.827 (17)	1.88 (2)	2.638 (3)	153 (3)
O11—H112···O5	0.82 (4)	2.21 (3)	2.981 (5)	157 (7)

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

The H atoms in the complexed and uncoordinated water molecules were located in a difference Fourier map, and restrained with O—H and H···H distances of 0.82 (2) and 1.39 (2) Å, respectively, with isotropic displacement parameters $1.2U_{\rm eq}$(O). Other H atoms were placed in calculated positions and constrained to ride on their parent atoms at distances of 0.99 (methylene) and 0.98 Å (methyl). Their isotropic displacement parameters were fixed at 1.2 or 1.5 (for methyl groups) times $U_{\rm eq}$(parent atom).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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