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Bis(μ-1,2,4-triazole-κ^2N^1:N^2)bis[diaqua(oxalato-κ^2O,O')copper(II)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.116
Data-to-parameter ratio = 18.6

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

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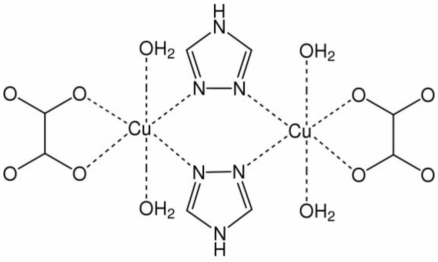
The crystal structure of the title compound, $[Cu_2(C_2O_4)_2(C_2H_3N_3)_2(H_2O)_4]$, consists of dimeric neutral entities with D_2 (222) point symmetry. The two Cu^{II} atoms (site symmetry 2) are linked by two symmetry-related N^1,N^2-bidentate 1,2,4-triazole bridges (one of the N atoms has site symmetry 2). The distorted octahedral coordination around each Cu atom is completed by two O donor atoms from a terminal bidentate oxalate ligand in the equatorial plane, and two *trans*-coordinated water molecules occupying the apical positions with longer metal–oxygen distances. The complete solid-state structure can be described as a three-dimensional supramolecular framework, stabilized by extensive hydrogen-bonding interactions involving the water molecules, the non-coordinated oxalate O atoms and the protonated N atom of the triazole ligands. The thermal degradation of the title compound was carried out in air between 298 and 873 K.

Comment

The design and synthesis of metal complexes with 1,2,4-triazole and its derivatives have attracted the interest of both physicists and chemists, due to their applications in the photographic (Berthaller, 1996) and anticorrosive industries (Tsarenko *et al.*, 1997) and the multiple coordination modes of these bridging ligands (through -κ^2N^1,N^2, -κ^2N^1,N^4 and -κ^3N^1,N^2,N^4 modes as anions) which have allowed the design of a great diversity of homo- and heteropolymetallic frameworks (Haasnoot, 2000) with remarkable magnetic properties (Tang *et al.*, 2001). In the framework of our current research on oxalate-containing first-row transition metal complexes (Castillo, Luque, Román *et al.*, 2001; Castillo *et al.*, 2003), we have obtained the compound bis(μ-1,2,4-triazole-κN^1:N^2)bis[diaqua(oxalato-κ^2O,O')copper(II)], (I).



(I)

The crystal structure of (I) consists of dinuclear complexes in which the metal atoms occupy special positions with site symmetry 2 and the overall cluster has 222 symmetry about its central point. As shown in Fig. 1, the two Cu^{II} atoms are linked

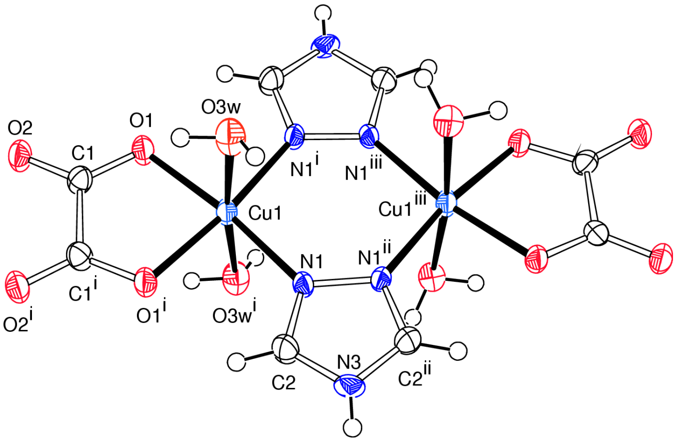
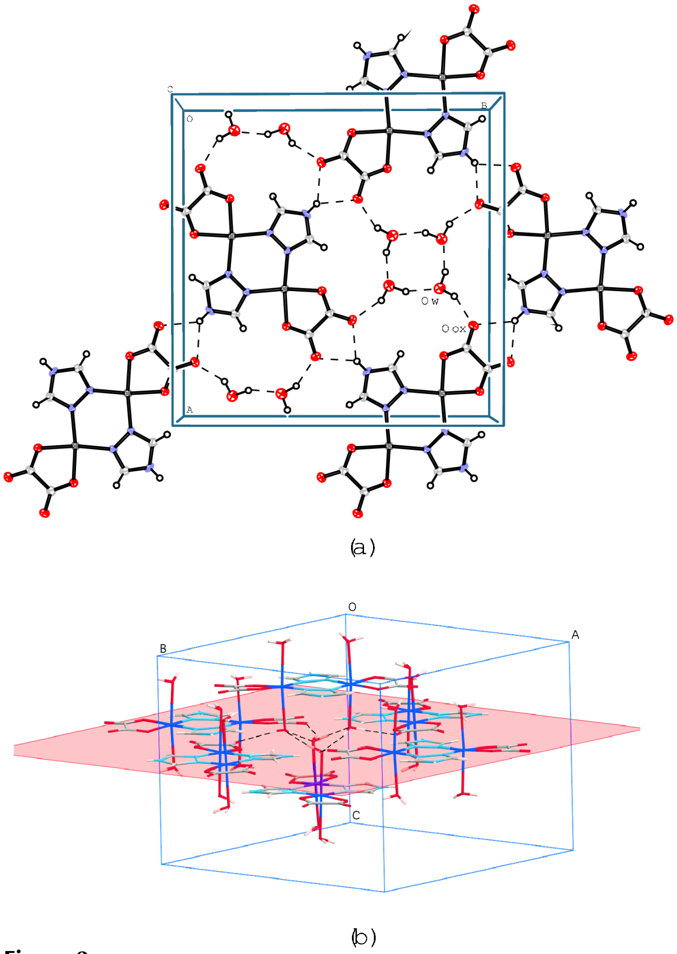


Figure 1
The dimeric unit of (I), showing the atom-numbering scheme, with 50% probability displacement ellipsoids. Symmetry codes as in Table 1; additionally (ii) $\frac{5}{4} - y, \frac{5}{4} - x, \frac{1}{4} - z$; (iii) $2 - x, \frac{1}{2} - y, z$.

by two bridging μ-1,2,4-triazole-$\kappa^2 N^1{:}N^2$ ligands, with a Cu—N—N bond angle of 129.9 (1)°. The Cu$\cdots$Cu^{iii} [symmetry code: (iii) $2 - x, \frac{1}{2} - y, z$] distance of 3.937 (1) Å is comparable to those in polymeric copper complexes containing metal centres linked by double triazole bridges (Liu *et al.*, 1999, 2003). The copper centres are also attached to two O atoms from a terminal oxalato anion which acts as a bidentate ligand. The O1—Cu—O1^i bond angle of 83.7 (1)° in the five-membered ring is within the range reported for copper(II) complexes containing bidentate oxalate ligands (Castillo, Luque & Román, 2001). The donor atoms of triazole and oxalate ligands establish short bond distances [Cu—O1 1.975 (2) Å and Cu—N1 2.002 (3) Å] and form the equatorial plane [maximum deviation from the least-squares plane is 0.052 (2) Å for atom O1] of the elongated CuN_2O_4 octahedron around each metal atom. The apical positions are occupied by the O atoms from two *trans*-coordinated water molecules, with a Cu—O3*w* bond distance of 2.483 (3) Å and an O3*w*—Cu—O3*w*^{i} bond angle of 174.6 (1)°. The 1,2,4-triazole and oxalate ligands are essentially planar [the maximum deviation is 0.049 (2) Å for atom O1]. The dihedral angle between the two bridging triazole ligands is 6.51 (4)°, while the oxalate and triazole ligands are tilted with respect to each other by 4.57 (3)°. The C—O bond distances of the oxalate O atoms attached to the Cu centres [1.259 (4) Å] are only slightly longer than those involving the non-coordinated O atoms [1.224 (4) Å], owing to the involvement of the free O atoms in an extensive network of hydrogen bonds.

In the crystal structure, the protonated N atoms of the dimeric entities form symmetric bifurcated N—H$\cdots$O$_{ox}$ hydrogen bonds with an adjacent unit to form square-grid sheets which extend parallel to the *ab* plane (Fig. 2). The holes generated by this packing are occupied by the coordinated water molecules belonging to dimeric units from adjacent sheets. These molecules are connected to each other and to the free oxalate O2 atom by means of O*w*—H*w*$\cdots$O*w* and O*w*—H*w*$\cdots$O$_{ox}$ hydrogen bonds, respectively.



(a)

(b)

Figure 2
Packing diagrams showing a fragment of the hydrogen-bonding network (dashed lines). In (*a*), O*w* water molecules belong to dimeric entities from adjacent layers. (*b*) Hydrogen-bond contacts between dimeric units belonging to adjacent layers.

The thermal degradation of (I) in air starts with an endothermic process in the temperature range 373–423 K, which is attributable to the loss of the coordinated water molecules (experimental 14.3%, calculated 14.0%). Subsequently, two exothermic processes in the temperature range 433–473 K lead to the intermediate compound $CuCO_3$ (experimental 51.6%, calculated 51.8%), which is stable up to 513 K. Finally, it undergoes successive exothermic processes to give CuO as the final product above 783 K (experimental 69.5%, calculated 69.3%).

Experimental

A methanolic solution (15 ml) of 1,2,4-triazole (0.082 g, 1.2 mmol) was slowly diffused into an aqueous solution (15 ml) of $K_2[Cu(\mu\text{-}C_2O_4)_2(H_2O)_2]$ (Kirschner, 1960) (0.106 g, 0.3 mmol) and $K_2(C_2O_4).H_2O$ (0.05 g, 0.27 mmol) using a test tube. Blue crystals of (I) were formed over a period of 3 weeks. Analysis calculated for $C_8H_{14}Cu_2N_6O_{12}$: C 18.7, H 2.8, N 16.4, Cu 24.8%; found: C 18.5, H 2.9, N 16.5, Cu 24.8%.

m10 Oscar Castillo *et al.* • $[Cu_2(C_2O_4)_2(C_2H_3N_3)_2(H_2O)_4]$ *Acta Cryst.* (2004). E**60**, m9–m11

Crystal data

$[Cu_2(C_2O_4)_2(C_2H_3N_3)_2(H_2O)_4]$
$M_r = 513.35$
Tetragonal, $I4_1/acd$
$a = 16.596$ (1) Å
$c = 11.996$ (2) Å
$V = 3304.0$ (6) Å^3
$Z = 8$
$D_x = 2.064$ Mg m^{-3}
$D_m = 2.05$ (1) Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
Mo $K\alpha$ radiation
Cell parameters from 13778 reflections
$\theta = 2.5$–$25.8°$
$\mu = 2.66$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.42 × 0.20 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2003)
$T_{min} = 0.534$, $T_{max} = 0.809$
13778 measured reflections
1212 independent reflections
652 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 30.0°$
$h = -23 \rightarrow 23$
$k = -23 \rightarrow 23$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.116$
$S = 0.98$
1212 reflections
65 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.975 (2)	Cu1—O3*w*	2.483 (3)
Cu1—N1	2.002 (3)		
O1—Cu1—O1^i	83.7 (1)	N1—Cu1—N1^i	100.0 (1)
O1—Cu1—N1	171.4 (1)	N1—Cu1—O3*w*	89.1 (1)
O1—Cu1—N1^i	88.3 (1)	N1—Cu1—O3*w*^{i}	87.5 (1)
O1—Cu1—O3*w*	94.0 (1)	O3*w*—Cu1—O3*w*^{i}	174.6 (1)
O1—Cu1—O3*w*^{i}	90.1 (1)		

Symmetry code: (i) $\frac{3}{4}+y, x-\frac{3}{4}, \frac{1}{4}-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2^{iv}	0.78	2.18	2.838 (4)	142
N3—H3···O2^{v}	0.78	2.18	2.838 (4)	142
O3*w*—H32···O2^{vi}	0.89	1.91	2.724 (3)	152
O3*w*—H31···O3*w*^{vii}	0.99	1.88	2.822 (4)	157

Symmetry codes: (iv) $\frac{1}{2}+x, -y, z$; (v) $\frac{5}{4}+y, \frac{3}{4}-x, \frac{1}{4}-z$; (vi) $\frac{3}{2}-x, y, -z$; (vii) $\frac{5}{4}-y, x-\frac{3}{4}, -\frac{1}{4}-z$.

All the H atoms were located in difference Fourier maps and were included in the structure-factor calculations with fixed positional parameters and a displacement parameter of $U_{iso} = 0.05$ Å^2.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RE*D (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Acta Cryst. (2004). E**60**, m9–m11 Oscar Castillo *et al.* • $[Cu_2(C_2O_4)_2(C_2H_3N_3)_2(H_2O)_4]$ **m11**