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μ-Oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$-bis[aqua(2,2′-bipyridyl-κ^2N,N')copper(II)] bis(hydrogen squarate)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.042
wR factor = 0.081
Data-to-parameter ratio = 18.4

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

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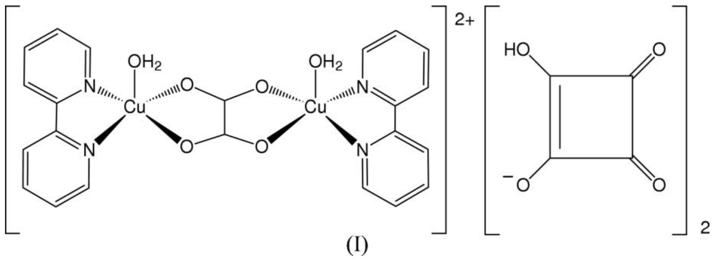
The title compound, $[Cu_2(C_2O_4)(C_{10}H_8N_2)_2(H_2O)_2](C_4HO_4)_2$, contains a dinuclear μ-oxalato–dicopper(II) complex cation in which the oxalate ligand (ox) bridges the Cu atoms in a bis-bidentate fashion. The square-pyramidal environment of each Cu atom is completed by the two N atoms of the 2,2′-bipyridine ligand (bpy) and by one apical water molecule. The hydrogen squarate counter-anions (Hsq) form cyclic dimeric units through strong O—H···O hydrogen bonds. The crystal structure shows alternating hydrogen-bonded complex cations and cyclic anionic units.

Comment

The remarkable ability of the oxalate bridge to mediate exchange coupling between first-row transition metal ions has attracted significant interest in the molecular magnetism area (Khan, 1993). Oxalato–copper(II) dinuclear complexes constitute one of the most deeply studied systems because of the strong magneto–structural correlations found (Cano *et al.*, 1998). Besides the series of compounds with general formula $[\{Cu(bpy)(H_2O)(X)\}_2(\mu\text{-ox})]\cdot[Cu(bpy)(ox)]$, X = NO_3^-, ClO_4^- and BF_4^- (Julve *et al.*, 1984; Gleizes *et al.*, 1992), the crystal structures of some complexes derived from $[\{Cu(bpy)\}_2(\mu\text{-ox})]^{2+}$ dinuclear cations have already been reported, such as the nitrate (Castillo *et al.*, 1999), chloride (Chattopadhyay *et al.*, 2002) and hexafluorophosphate (Thomas *et al.*, 2000). We report here the synthesis and crystal structure of the title new salt of the same dinuclear cation, $[\{Cu(bpy)(H_2O)\}_2(\mu\text{-ox})](Hsq)_2$, (I).



(I)

The asymmetric unit of (I) contains one $[\{Cu(bpy)(H_2O)\}_2(\mu\text{-ox})]^{2+}$ complex cation and two hydrogen squarate anions (Fig. 1). The complex cation consists of two Cu^{II} atoms bridged by an oxalate ligand in the usual bis-bidentate fashion, the Cu–ox–Cu framework displaying a boat conformation. The coordination geometry around each Cu^{II} atom is square-pyramidal, CuN_2O_3, with two O atoms of the ox bridge and two N atoms of the bpy ligand in the basal plane, and a water molecule in the apical position.

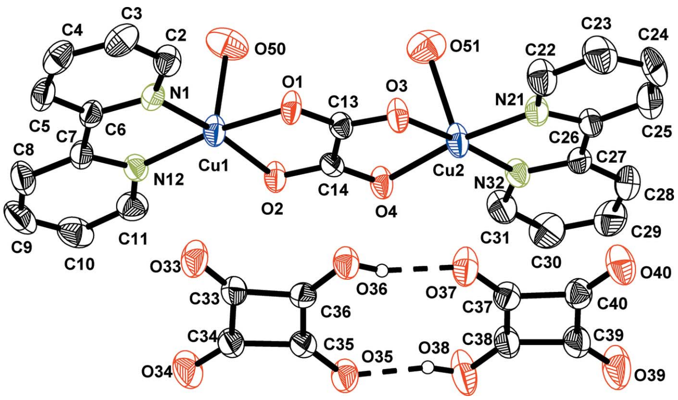


Figure 1
ORTEP-3 plot of (I) (50% probability displacement ellipsoids). Aromatic H atoms have been omitted for clarity. Dashed lines indicate hydrogen bonds.

The hydrogen squarate counter-anions form cyclic dimeric units through strong O—H$\cdots$O hydrogen bonds. The crystal structure shows alternating complex cations and cyclic anionic units, arranged in two different levels and linked through an extended network of O(water)—H$\cdots$O(Hsq) hydrogen bonds (Table 2). They are further connected by means of π stacking interactions, involving the N1/C6 and C27/N32 bipyridine rings, and C(bpy)—H$\cdots$O(Hsq) hydrogen bonds, giving rise to layers parallel to the $(\overline{1}1\overline{1})$ plane (Fig. 2).

Experimental

A solution of squaric acid (23 mg) in water (20 ml) was added to a solution containing $CuCl_2\cdot 2H_2O$ (68 mg), 2,2′-bipyridine (62 mg) and oxalic acid (25 mg) in water (30 ml) and methanol (10 ml). Single crystals of the title compound suitable for X-ray diffraction were obtained by slow evaporation of the reaction mixture. Elemental analysis found: C 45.42, H 2.86, N 7.04%; calculated for $C_{30}Cu_2H_{22}N_4O_{14}$: C 45.63, H 2.81, N 7.10%.

Crystal data

$[Cu_2(C_2O_4)(C_{10}H_8N_2)_2(H_2O)_2](C_4HO_4)_2$
$M_r = 789.62$
Triclinic, $P\overline{1}$
$a = 8.0147$ (12) Å
$b = 9.2276$ (12) Å
$c = 21.728$ (2) Å
$\alpha = 92.049$ (10)°
$\beta = 94.860$ (11)°
$\gamma = 109.283$ (12)°
$V = 1507.9$ (4) Å^3
$Z = 2$
$D_x = 1.739$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6000 reflections
$\theta = 3.5$–25°
$\mu = 1.49$ mm^{-1}
$T = 295$ (2) K
Prism, blue
0.14 × 0.09 × 0.07 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
$T_{\min} = 0.719$, $T_{\max} = 0.843$
14798 measured reflections
8613 independent reflections
3850 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 30°$
$h = -8 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -30 \rightarrow 30$

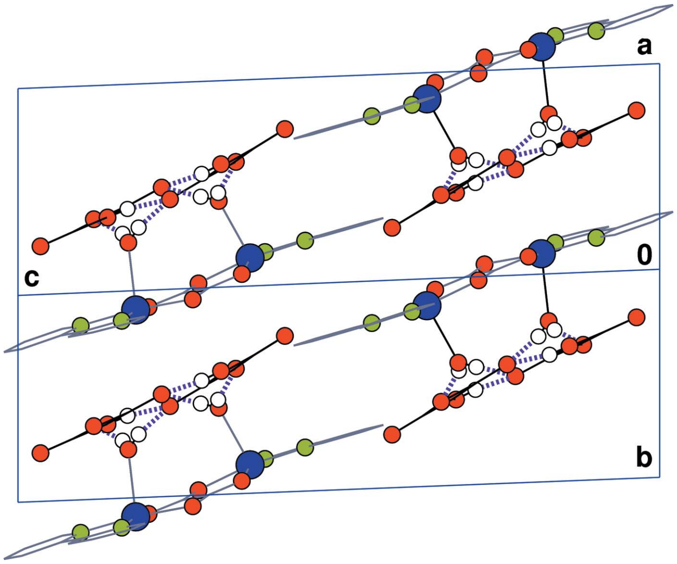


Figure 2
View of the crystal packing along the [110] direction. Dashed lines indicate O—H$\cdots$O hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.081$
$S = 0.76$
8613 reflections
469 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.958 (2)	C34—C35	1.494 (4)
Cu1—N12	1.969 (2)	C35—O35	1.253 (3)
Cu1—O1	1.9775 (17)	C35—C36	1.411 (4)
Cu1—O2	1.9644 (17)	C36—O36	1.297 (3)
Cu1—O50	2.219 (3)	C36—C33	1.435 (4)
Cu2—N21	1.957 (2)	C37—O37	1.256 (3)
Cu2—N32	1.954 (2)	C37—C38	1.417 (4)
Cu2—O3	1.9746 (17)	C38—O38	1.295 (3)
Cu2—O4	1.9778 (17)	C38—C39	1.453 (4)
Cu2—O51	2.277 (3)	C39—O39	1.213 (3)
C33—O33	1.223 (3)	C39—C40	1.510 (4)
C33—C34	1.497 (4)	C40—O40	1.212 (3)
C34—O34	1.219 (3)	C40—C37	1.483 (4)
N1—Cu1—N12	82.36 (9)	N21—Cu2—N32	82.50 (9)
N1—Cu1—O2	171.31 (8)	N21—Cu2—O4	171.87 (9)
N1—Cu1—O50	99.90 (9)	N21—Cu2—O51	99.52 (9)
N12—Cu1—O1	168.28 (8)	N32—Cu2—O3	174.38 (9)
N12—Cu1—O50	100.62 (9)	N32—Cu2—O51	99.76 (9)
O1—Cu1—O2	85.40 (7)	O3—Cu2—O4	85.50 (7)
O1—Cu1—O50	91.04 (9)	O3—Cu2—O51	85.84 (9)
O2—Cu1—O50	88.79 (9)	O4—Cu2—O51	88.33 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O36—H36···O37	0.79 (4)	1.75 (4)	2.517 (3)	164 (4)
O38—H38···O35	0.79 (4)	1.77 (4)	2.546 (3)	166 (4)
O50—H50*A*···O34^{i}	0.72 (2)	2.03 (2)	2.711 (3)	158 (4)
O50—H50*B*···O37^{ii}	0.72 (3)	2.05 (3)	2.737 (3)	161 (4)
O51—H51*A*···O35^{i}	0.72 (3)	2.07 (3)	2.758 (3)	161 (4)
O51—H51*B*···O40^{ii}	0.72 (3)	2.03 (3)	2.722 (3)	164 (4)
C2—H2···O1	0.93	2.52	3.037 (3)	115
C3—H3···O33^{iii}	0.93	2.39	3.296 (4)	166
C5—H5···O34^{iv}	0.93	2.52	3.360 (4)	151
C8—H8···O33^{iv}	0.93	2.47	3.198 (4)	136
C25—H25···O39^{v}	0.93	2.42	3.153 (4)	136
C30—H30···O39^{vi}	0.93	2.37	3.284 (4)	169
C31—H31···O4	0.93	2.50	3.021 (3)	116

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

The H atoms of the water molecules and hydrogen squarate anions were located in a Fourier difference map. All remaining H atoms were positioned geometrically. Hydrogen squarate and water H atoms were refined freely, except that all water O—H distances were restrained to be equal to within 0.01 Å. All remaining H atoms were refined as riding, with isotropic displacement parameters fixed at 1.2 times U_{eq} of their parent atoms.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2003); data reduction: *CrysAlisRED*; program(s) used to solve structure: *DIRDIF99.2* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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