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Bis(4-aminopyridinium) bis(oxalato-κ^2O,O')cuprate(II) dihydrate

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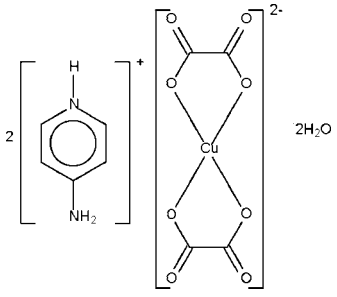
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.037; wR factor = 0.109; data-to-parameter ratio = 10.4.

The Cu^{II} atom in the title salt, $(C_5H_7N_2)_2[Cu(C_2O_4)_2]\cdot 2H_2O$, is located on a center of inversion and is chelated by two oxalate groups in a square-planar coordination geometry. The cation, anion and water molecules interact through hydrogen bonds, forming a three-dimensional hydrogen-bonded network.

Related literature

See Geiser *et al.* (1987) for the square-planar pyridinium dioxalatocuprate(II) oxalic acid co-crystal. See Sun *et al.* (2004) for 2,6-bis(4′-pyridyl-1′-pyridinium)pyrazine bis(bis(-oxalato)cuprate(II), which is also square planar. In bis(2-aminoanilinium) bis(oxalato)cuprate(II), the amino groups coordinate to the metal atom, which exhibits octahedral coordination (Keene *et al.*, 2003).



Experimental

Crystal data

$(C_5H_7N_2)_2[Cu(C_2O_4)_2]\cdot 2H_2O$
M_r = 465.86
Monoclinic, $P2_1/c$
a = 3.7105 (3) Å
b = 20.311 (1) Å
c = 11.9261 (9) Å
β = 90.450 (1)°
V = 898.8 (1) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.28 mm^{-1}
T = 295 (2) K
0.14 × 0.10 × 0.08 mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.764, T_{max} = 0.905
2623 measured reflections
1590 independent reflections
1498 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.109
S = 1.12
1590 reflections
153 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.932 (2)	Cu1—O3	1.927 (2)
O1—Cu1—O3	85.4 (1)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H11···O1	0.85 (3)	2.03 (2)	2.852 (3)	164 (5)
O1w—H12···O3^{i}	0.85 (3)	2.12 (5)	2.931 (3)	160 (5)
N1—H1···O2	0.85 (3)	2.12 (2)	2.858 (4)	146 (4)
N2—H21···O4^{ii}	0.85 (1)	2.07 (1)	2.906 (4)	168 (4)
N2—H22···O1w^{iii}	0.85 (3)	2.02 (3)	2.867 (4)	176 (4)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+3, -y+1, -z$.

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: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2384).

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supporting information

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S1. Comment

There are many crystallographic studies of coordination compounds of oxalic acid (Cambridge Structural Database, Version 5.28, Nov. 2006). The copper(II) center in the title compound shows square-planar coordination (Table 1); the cations, anions and lattice water molecules interact through hydrogen bonds (Table 2) to give rise to a three-dimensional network motif.

S2. Experimental

Potassium oxalate monohydrate (0.036 g, 0.2 mmol) dissolved in water (5 ml) was reacted with copper nitrate trihydrate (0.048 g, 0.2 mmol) in water (5 ml). To this solution was added 4-C_5H_4N–NH–C(O)–C(O)–NH–4–C_5H_4N (0.048 g, 0.2 mmol) dissolved in methanol (15 ml). Blue crystals separated after a few days in 60% yield. CH&N elemental analysis. Calc. for $C_{14}H_{18}CuN_4O_{10}$: C 36.09, H 3.89, N 12.02%. Found: C 36.43, H 3.74, N 12.18%.

S3. Refinement

The carbon-bound H atoms were placed in calculated positions and were allowed to ride on the parent atoms. The oxygen- and nitrogen-bound H atoms were refined with a distance restraint O–H = N–H = 0.85±0.01 Å. Their temperature factors were freely refined.

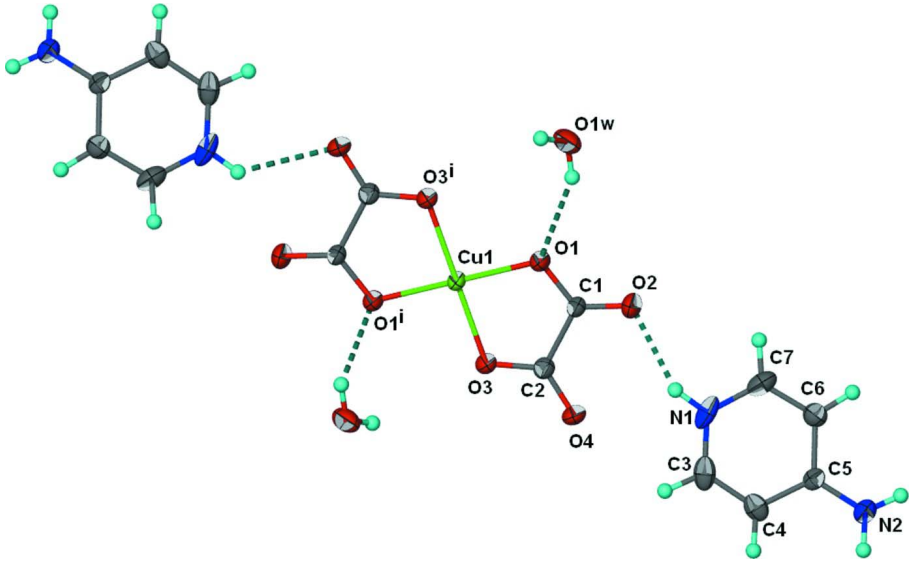

Figure 1

Thermal ellipsoid plot of $2[C_5H_7N_2]^+[Cu(C_2O_4)_2]^{2-}\cdot 2H_2O$; Displacement ellipsoids are drawn at the 50% probability level, and H atoms as spheres of arbitrary radii.

Bis(4-aminopyridinium) bis(oxalato-κ^2O,O')cuprate(II) dihydrate

Crystal data

$(C_5H_7N_2)_2[Cu(C_2O_4)_2]\cdot 2H_2O$
$M_r = 465.86$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 3.7105$ (3) Å
$b = 20.311$ (1) Å
$c = 11.9261$ (9) Å
$\beta = 90.450$ (1)°
$V = 898.8$ (1) Å^3
$Z = 2$
$F(000) = 478$
$D_x = 1.721$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2198 reflections
$\theta = 2.0$–$25.1°$
$\mu = 1.28$ mm^{-1}
$T = 295$ K
Block, blue
0.14 × 0.10 × 0.08 mm

Data collection

Bruker SMART area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.764$, $T_{max} = 0.905$
2623 measured reflections
1590 independent reflections
1498 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 25.1°$, $\theta_{min} = 2.0°$
$h = -4\rightarrow4$
$k = -21\rightarrow24$
$l = -8\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.109$
$S = 1.12$
1590 reflections
153 parameters
5 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 1.2237P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.5000	0.5000	0.5000	0.0283 (2)
O1	0.8063 (6)	0.52464 (11)	0.37661 (18)	0.0352 (5)
O2	1.0084 (7)	0.48225 (12)	0.21648 (19)	0.0399 (6)
O3	0.4985 (6)	0.41370 (10)	0.43287 (17)	0.0313 (5)
O4	0.7190 (7)	0.36328 (11)	0.28166 (19)	0.0386 (5)
O1w	1.1418 (8)	0.65099 (13)	0.3772 (2)	0.0477 (6)
N1	1.1417 (8)	0.37249 (17)	0.0727 (2)	0.0439 (7)
N2	1.5342 (8)	0.27528 (14)	−0.1995 (2)	0.0365 (6)
C1	0.8457 (8)	0.47791 (15)	0.3044 (2)	0.0275 (6)
C2	0.6748 (8)	0.41168 (14)	0.3400 (2)	0.0275 (6)
C3	1.1500 (8)	0.3067 (2)	0.0721 (3)	0.0411 (8)
H3	1.0674	0.2837	0.1343	0.049*

C4	1.2757 (8)	0.27283 (17)	−0.0171 (3)	0.0354 (7)
H4	1.2776	0.2270	−0.0160	0.043*
C5	1.4040 (7)	0.30699 (15)	−0.1115 (2)	0.0266 (6)
C6	1.3848 (8)	0.37643 (16)	−0.1090 (3)	0.0344 (7)
H6	1.4609	0.4011	−0.1702	0.041*
C7	1.2545 (9)	0.40679 (17)	−0.0167 (3)	0.0428 (8)
H7	1.2429	0.4525	−0.0151	0.051*
H11	1.045 (13)	0.6140 (13)	0.363 (4)	0.084 (17)*
H12	1.268 (11)	0.642 (3)	0.434 (3)	0.077 (17)*
H1	1.068 (10)	0.3915 (18)	0.132 (2)	0.046 (11)*
H21	1.563 (10)	0.2337 (6)	−0.199 (3)	0.042 (10)*
H22	1.621 (11)	0.2979 (18)	−0.253 (2)	0.055 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0380 (3)	0.0234 (3)	0.0237 (3)	−0.00362 (19)	0.0082 (2)	−0.00456 (18)
O1	0.0493 (13)	0.0257 (11)	0.0309 (11)	−0.0074 (10)	0.0139 (10)	−0.0061 (9)
O2	0.0526 (14)	0.0358 (12)	0.0314 (12)	−0.0023 (11)	0.0165 (11)	−0.0029 (10)
O3	0.0416 (12)	0.0258 (11)	0.0265 (11)	−0.0047 (9)	0.0058 (9)	−0.0030 (8)
O4	0.0550 (14)	0.0256 (11)	0.0354 (12)	−0.0043 (10)	0.0117 (10)	−0.0088 (9)
O1w	0.0663 (17)	0.0358 (14)	0.0411 (14)	−0.0106 (12)	−0.0018 (13)	0.0083 (11)
N1	0.0379 (15)	0.064 (2)	0.0295 (15)	0.0085 (14)	−0.0009 (12)	−0.0171 (14)
N2	0.0476 (16)	0.0320 (15)	0.0300 (14)	0.0043 (12)	0.0065 (12)	−0.0016 (12)
C1	0.0325 (15)	0.0265 (15)	0.0236 (15)	0.0023 (12)	0.0016 (12)	−0.0007 (11)
C2	0.0310 (14)	0.0277 (15)	0.0240 (14)	0.0019 (11)	0.0004 (12)	−0.0020 (12)
C3	0.0321 (16)	0.065 (2)	0.0265 (16)	0.0059 (15)	−0.0001 (13)	0.0060 (16)
C4	0.0328 (15)	0.0393 (17)	0.0342 (16)	0.0024 (13)	−0.0023 (13)	0.0077 (14)
C5	0.0248 (13)	0.0307 (15)	0.0244 (14)	0.0030 (11)	−0.0051 (11)	−0.0015 (12)
C6	0.0353 (16)	0.0330 (16)	0.0348 (17)	0.0010 (13)	0.0012 (13)	0.0021 (13)
C7	0.0436 (18)	0.0353 (18)	0.049 (2)	0.0056 (14)	−0.0018 (16)	−0.0133 (16)

Geometric parameters (Å, º)

Cu1—O1	1.932 (2)	N2—C5	1.325 (4)
Cu1—O3	1.927 (2)	N2—H21	0.85 (1)
Cu1—O3^{i}	1.927 (2)	N2—H22	0.85 (3)
Cu1—O1^{i}	1.932 (2)	C1—C2	1.548 (4)
O1—C1	1.290 (4)	C3—C4	1.352 (5)
O2—C1	1.217 (4)	C3—H3	0.9300
O3—C2	1.291 (4)	C4—C5	1.409 (4)
O4—C2	1.216 (4)	C4—H4	0.9300
O1w—H11	0.85 (3)	C5—C6	1.413 (4)
O1w—H12	0.85 (3)	C6—C7	1.355 (5)
N1—C3	1.337 (5)	C6—H6	0.9300
N1—C7	1.343 (5)	C7—H7	0.9300
N1—H1	0.85 (3)		

O3—Cu1—O3^{i}	180	O4—C2—O3	126.0 (3)
O3—Cu1—O1^{i}	94.7 (1)	O4—C2—C1	119.2 (3)
O3^{i}—Cu1—O1^{i}	85.4 (1)	O3—C2—C1	114.8 (2)
O1—Cu1—O3	85.4 (1)	N1—C3—C4	121.4 (3)
O3^{i}—Cu1—O1	94.7 (1)	N1—C3—H3	119.3
O1^{i}—Cu1—O1	180	C4—C3—H3	119.3
C1—O1—Cu1	112.83 (19)	C3—C4—C5	119.9 (3)
C2—O3—Cu1	112.66 (18)	C3—C4—H4	120.0
H11—O1w—H12	101 (5)	C5—C4—H4	120.0
C3—N1—C7	120.4 (3)	N2—C5—C4	121.4 (3)
C3—N1—H1	118 (3)	N2—C5—C6	121.4 (3)
C7—N1—H1	122 (3)	C4—C5—C6	117.2 (3)
C5—N2—H21	122 (3)	C7—C6—C5	119.3 (3)
C5—N2—H22	118 (3)	C7—C6—H6	120.3
H21—N2—H22	120 (4)	C5—C6—H6	120.3
O2—C1—O1	125.5 (3)	N1—C7—C6	121.7 (3)
O2—C1—C2	120.4 (3)	N1—C7—H7	119.2
O1—C1—C2	114.0 (2)	C6—C7—H7	119.2
O3—Cu1—O1—C1	5.3 (2)	O2—C1—C2—O3	−177.7 (3)
O3^{i}—Cu1—O1—C1	−174.7 (2)	O1—C1—C2—O3	4.2 (4)
O1^{i}—Cu1—O3—C2	177.2 (2)	C7—N1—C3—C4	1.0 (5)
O1—Cu1—O3—C2	−2.8 (2)	N1—C3—C4—C5	0.5 (5)
Cu1—O1—C1—O2	175.7 (3)	C3—C4—C5—N2	178.9 (3)
Cu1—O1—C1—C2	−6.3 (3)	C3—C4—C5—C6	−1.7 (4)
Cu1—O3—C2—O4	179.1 (3)	N2—C5—C6—C7	−179.1 (3)
Cu1—O3—C2—C1	0.2 (3)	C4—C5—C6—C7	1.6 (4)
O2—C1—C2—O4	3.3 (4)	C3—N1—C7—C6	−1.1 (5)
O1—C1—C2—O4	−174.8 (3)	C5—C6—C7—N1	−0.2 (5)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H11···O1	0.85 (3)	2.03 (2)	2.852 (3)	164 (5)
O1*w*—H12···O3^{ii}	0.85 (3)	2.12 (5)	2.931 (3)	160 (5)
N1—H1···O2	0.85 (3)	2.12 (2)	2.858 (4)	146 (4)
N2—H21···O4^{iii}	0.85 (1)	2.07 (1)	2.906 (4)	168 (4)
N2—H22···O1*w*^{iv}	0.85 (3)	2.02 (3)	2.867 (4)	176 (4)

Symmetry codes: (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*+1, −*y*+1/2, *z*−1/2; (iv) −*x*+3, −*y*+1, −*z*.