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4,4'-Bipyridinium bis(oxalato- κ^2O^1, O^2)-cuprate(II): an ion-pair complexLai-Jun Zhang,^{a,b*} Xing-Can Shen^c and Hong Liang^c

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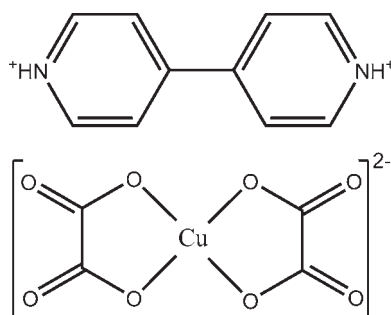
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.027; wR factor = 0.073; data-to-parameter ratio = 10.2.

The title compound, $(C_{10}H_{10}N_2)[Cu(C_2O_4)_2]$ or $(4,4'-H_2bpy)^+ [Cu(ox)_2]^{2-}$ (bpy is 4,4'-bipyridine and ox is oxalate), is an ion-pair complex comprising a protonated 4,4'-bipyridinium dication and a square-planar dioxalato-copper(II) dianion. In the centrosymmetric dianion, the Cu^{II} centre is coordinated by four O atoms from the two discrete oxalate ligands [$Cu-O = 1.9245$ (19) and 1.9252 (17) Å], while the planar dications are also centrosymmetric. Inter-species $N-H \cdots O$ hydrogen bonds link the cations and anions into one-dimensional chains and, together with weak intra-ion $C-H \cdots O$ interactions, give a two-dimensional sheet structure.

Related literature

For related background, see: Ren *et al.* (2007). For related structures, see, for example: Bukowska-Strzyzewska & Tosik (1979); Crawford *et al.* (2004); Diallo *et al.* (2008); Dou *et al.* (2007); Madhu & Das (2004); Näther *et al.* (2001); Tosik *et al.* (1990); Willett *et al.* (2006).



Experimental

Crystal data

$(C_{10}H_{10}N_2)[Cu(C_2O_4)_2]$
 $M_r = 397.79$
 Triclinic, $P\bar{1}$
 $a = 3.6900$ (7) Å
 $b = 9.950$ (2) Å
 $c = 10.230$ (2) Å
 $\alpha = 113.77$ (3)°
 $\beta = 98.43$ (3)°

$\gamma = 97.89$ (3)°
 $V = 331.93$ (15) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.70$ mm⁻¹
 $T = 293$ K
 $0.41 \times 0.27 \times 0.22$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{min} = 0.527$, $T_{max} = 0.705$

1761 measured reflections
 1168 independent reflections
 1126 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.09$
 1168 reflections

115 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.30$ e Å⁻³
 $\Delta\rho_{min} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O4^i$	0.86	2.02	2.755 (3)	143
$N1-H1A \cdots O1^i$	0.86	2.21	2.880 (3)	135
$C1-H1 \cdots O4^{ii}$	0.93	2.49	3.381 (3)	160
$C2-H2 \cdots O3^{ii}$	0.93	2.57	3.195 (3)	125
$C4-H4 \cdots O2$	0.93	2.42	3.272 (3)	153
$C5-H5 \cdots O1$	0.93	2.46	3.215 (3)	138

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2005); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2010).

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supplementary materials

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4,4'-Bipyridinium bis(oxalato- κ^2O^1,O^2)cuprate(II): an ion-pair complex

L.-J. Zhang, X.-C. Shen and H. Liang

Comment

Currently, *in situ* chemical reactions are of considerable interest, providing a powerful route for the preparation of novel crystals with unexpected structures, e.g. Ren *et al.* (2007) has reported the hydrothermal synthesis of a new coordination polymer $[\text{Cu}(\text{ox})(4,4'\text{-bpy})]_n$ (bpy = 4,4'-bipyridine; ox = oxalate²⁻) resulting from the decomposition of furan-2-carboxylic acid to give the ox²⁻ ligand in the reaction of this acid with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 4,4'-bpy. In the work reported here, a novel ion-pair complex, $(4,4'\text{-H}_2\text{bpy})[\text{Cu}(\text{ox})_2]$ (I) was obtained by using sodium 2-hydroxyphosphonocarboxylate as the ox²⁻ source and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as the copper source. Copper(II) is a relatively strong oxidant with the ability to oxidise the sodium 2-hydroxyphosphonocarboxylic giving ox²⁻ which is generated *in situ*, resulting in formation of the title compound, the structure of which is reported here.

The structure of the (I) shows an ion-pair complex comprising a protonated 4,4'-bipyridine dication, $(4,4'\text{-H}_2\text{bpy})^{2+}$ (Bukowska-Strzyzewska *et al.*, 1979; Crawford *et al.*, 2004; Dou *et al.*, 2007; Madhu *et al.*, 2004; Näther *et al.*, 2001; Tosik *et al.*, 1990; Willett *et al.*, 2006), and a $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ anion (Fig. 1). The discrete bis-(oxalato)copper(II) dianions have square planar CuO_4 stereochemistry, comprising four O donor atoms from two oxalate ligands [Cu–O, 1.9245 (19), 1.9252 (17) Å] and lie across inversion centres in the unit cell. In the axial sites, the Cu–O_{oxalate} contacts are 2.920 (2) Å. With the 4,4'-bipyridine dications, the pyridine rings are coplanar and also have crystallographic inversion symmetry. Interamolecular N—H \cdots O hydrogen bonds (Table 1) link the cations and anions into one-dimensional chains and together with weak intramolecular C—H \cdots O interactions give two-dimensional sheet structures which layer down the *a* direction in the unit cell (Fig. 2).

Experimental

Sodium 2-hydroxyphosphonocarboxylate (1 mmol) was dissolved in 10 ml of 50% ethanol-water after which 1 mmol of copper(II) chloride dihydrate and 1 mmol of 4,4'-bipyridine were added in sequence. After stirring for 10 min, the resulting mixture was transferred into a Teflon-lined stainless steel vessel (15 ml) which was sealed and heated at 110 °C for four days, then allowed to cool to room temperature. The blue-green single crystal blocks of the title compound (I), together with yellow-red prismatic crystals of a second unidentified component were obtained. The yield of (I) was *ca.* 25% (based on copper). IR (cm⁻¹, KBr): 3439, 3110, 3060, 2921, 1665, 1581, 1487, 1409, 1273, 1205 1106, 1000, 892, 827, 798.

Refinement

All H atoms were geometrically placed and refined using a riding model approximation, with C—H = 0.93 Å or N—H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Figures

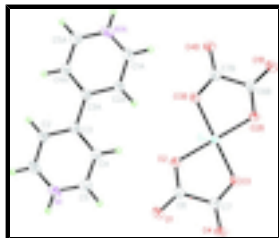


Fig. 1. Molecular configuration and atom numbering scheme for the discrete dication and dianion species in (I). Displacement ellipsoids are drawn at the 50% probability level. Both cation and anion have crystallographic inversion symmetry. Symmetry codes: (A) $-x + 1, -y, -z$; (B) $-x, -y, -z + 1$.

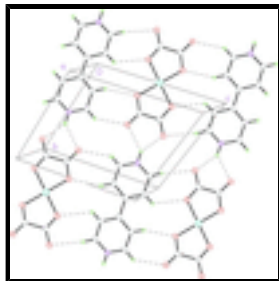


Fig. 2. The two-dimensional hydrogen-bonded sheet structure of (I) showing intra- and intermolecular hydrogen bonds as dashed lines.

4,4'-Bipyridinium bis(oxalato- κ^2O^1, O^2)cuprate(II)

Crystal data

(C₁₀H₁₀N₂)[Cu(C₂O₄)₂]

$M_r = 397.79$

Triclinic, PT

Hall symbol: $-P\ 1$

$a = 3.6900\ (7)\ \text{\AA}$

$b = 9.950\ (2)\ \text{\AA}$

$c = 10.230\ (2)\ \text{\AA}$

$\alpha = 113.77\ (3)^\circ$

$\beta = 98.43\ (3)^\circ$

$\gamma = 97.89\ (3)^\circ$

$V = 331.93\ (15)\ \text{\AA}^3$

$Z = 1$

$F_{000} = 201$

$D_x = 1.990\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1168 reflections

$\theta = 2.2\text{--}25.1^\circ$

$\mu = 1.70\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, green-blue

$0.41 \times 0.27 \times 0.22\ \text{mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ \text{K}$

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2005)

$T_{\min} = 0.527, T_{\max} = 0.705$

1761 measured reflections

1168 independent reflections

1126 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\max} = 25.1^\circ$

$\theta_{\min} = 2.2^\circ$

$h = -4 \rightarrow 4$

$k = -9 \rightarrow 11$

$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.073$	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.1814P]$
$S = 1.09$	where $P = (F_o^2 + 2F_c^2)/3$
1168 reflections	$(\Delta/\sigma)_{\max} < 0.001$
115 parameters	$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.0000	0.0000	0.5000	0.02273 (16)
C1	0.9693 (6)	0.2924 (3)	0.0264 (3)	0.0263 (5)
H1	1.0658	0.3392	-0.0273	0.032*
C2	0.7599 (6)	0.1481 (3)	-0.0443 (3)	0.0228 (5)
H2	0.7140	0.0971	-0.1459	0.027*
C3	0.6154 (6)	0.0779 (2)	0.0367 (2)	0.0182 (4)
C4	0.6955 (7)	0.1599 (3)	0.1887 (3)	0.0265 (5)
H4	0.6054	0.1165	0.2461	0.032*
C5	0.9057 (7)	0.3037 (3)	0.2534 (3)	0.0312 (6)
H5	0.9580	0.3582	0.3547	0.037*
C6	0.4733 (6)	0.2586 (3)	0.5616 (3)	0.0232 (5)
C7	0.3414 (6)	0.2770 (3)	0.7045 (2)	0.0224 (5)
N1	1.0353 (5)	0.3657 (2)	0.1713 (2)	0.0273 (4)
H1A	1.1664	0.4564	0.2135	0.033*
O1	0.6801 (5)	0.3636 (2)	0.5609 (2)	0.0342 (4)
O2	0.3514 (5)	0.12699 (19)	0.45407 (17)	0.0286 (4)
O3	0.1187 (5)	0.16185 (19)	0.69418 (18)	0.0265 (4)
O4	0.4569 (5)	0.39568 (19)	0.81441 (18)	0.0313 (4)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0285 (2)	0.0171 (2)	0.0166 (2)	-0.00496 (16)	0.00626 (16)	0.00411 (17)
C1	0.0250 (12)	0.0251 (12)	0.0318 (13)	0.0015 (10)	0.0060 (10)	0.0167 (11)
C2	0.0249 (11)	0.0219 (12)	0.0211 (11)	0.0009 (9)	0.0046 (9)	0.0102 (10)
C3	0.0155 (10)	0.0184 (11)	0.0216 (11)	0.0041 (9)	0.0043 (8)	0.0095 (9)
C4	0.0319 (13)	0.0245 (12)	0.0218 (12)	-0.0003 (10)	0.0082 (10)	0.0101 (10)
C5	0.0360 (14)	0.0262 (13)	0.0237 (13)	-0.0002 (11)	0.0047 (10)	0.0059 (11)
C6	0.0244 (11)	0.0224 (12)	0.0214 (12)	0.0018 (9)	0.0051 (9)	0.0092 (10)
C7	0.0235 (11)	0.0221 (12)	0.0208 (12)	0.0022 (9)	0.0046 (9)	0.0096 (10)
N1	0.0242 (10)	0.0160 (10)	0.0371 (12)	-0.0022 (8)	0.0040 (9)	0.0099 (9)
O1	0.0425 (10)	0.0237 (9)	0.0309 (10)	-0.0083 (8)	0.0111 (8)	0.0101 (8)
O2	0.0381 (9)	0.0205 (8)	0.0196 (8)	-0.0057 (7)	0.0102 (7)	0.0037 (7)
O3	0.0332 (9)	0.0208 (8)	0.0198 (8)	-0.0059 (7)	0.0079 (7)	0.0062 (7)
O4	0.0389 (10)	0.0203 (9)	0.0227 (9)	-0.0070 (7)	0.0063 (7)	0.0018 (7)

Geometric parameters (\AA , $^\circ$)

Cu1—O3	1.9245 (19)	C4—C5	1.367 (4)
Cu1—O3 ⁱ	1.9245 (19)	C4—H4	0.9300
Cu1—O2 ⁱ	1.9252 (17)	C5—N1	1.331 (3)
Cu1—O2	1.9252 (17)	C5—H5	0.9300
C1—N1	1.327 (3)	C6—O1	1.210 (3)
C1—C2	1.369 (3)	C6—O2	1.288 (3)
C1—H1	0.9300	C6—C7	1.557 (3)
C2—C3	1.397 (3)	C7—O4	1.221 (3)
C2—H2	0.9300	C7—O3	1.272 (3)
C3—C4	1.395 (3)	N1—H1A	0.8600
C3—C3 ⁱⁱ	1.485 (4)		
O3—Cu1—O3 ⁱ	180.0	C5—C4—H4	119.9
O3—Cu1—O2 ⁱ	93.91 (7)	C3—C4—H4	119.9
O3 ⁱ —Cu1—O2 ⁱ	86.09 (7)	N1—C5—C4	119.9 (2)
O3—Cu1—O2	86.09 (7)	N1—C5—H5	120.1
O3 ⁱ —Cu1—O2	93.91 (7)	C4—C5—H5	120.1
O2 ⁱ —Cu1—O2	180.00 (8)	O1—C6—O2	126.2 (2)
N1—C1—C2	120.4 (2)	O1—C6—C7	119.2 (2)
N1—C1—H1	119.8	O2—C6—C7	114.60 (19)
C2—C1—H1	119.8	O4—C7—O3	125.9 (2)
C1—C2—C3	119.7 (2)	O4—C7—C6	119.3 (2)
C1—C2—H2	120.1	O3—C7—C6	114.8 (2)
C3—C2—H2	120.1	C1—N1—C5	122.3 (2)
C4—C3—C2	117.5 (2)	C1—N1—H1A	118.9
C4—C3—C3 ⁱⁱ	121.4 (2)	C5—N1—H1A	118.9
C2—C3—C3 ⁱⁱ	121.1 (3)	C6—O2—Cu1	111.74 (14)
C5—C4—C3	120.3 (2)	C7—O3—Cu1	112.38 (14)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O4 ⁱⁱⁱ	0.86	2.02	2.755 (3)	143
N1—H1A \cdots O1 ⁱⁱⁱ	0.86	2.21	2.880 (3)	135
C1—H1 \cdots O4 ^{iv}	0.93	2.49	3.381 (3)	160
C2—H2 \cdots O3 ^{iv}	0.93	2.57	3.195 (3)	125
C4—H4 \cdots O2	0.93	2.42	3.272 (3)	153
C5—H5 \cdots O1	0.93	2.46	3.215 (3)	138

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

Fig. 1

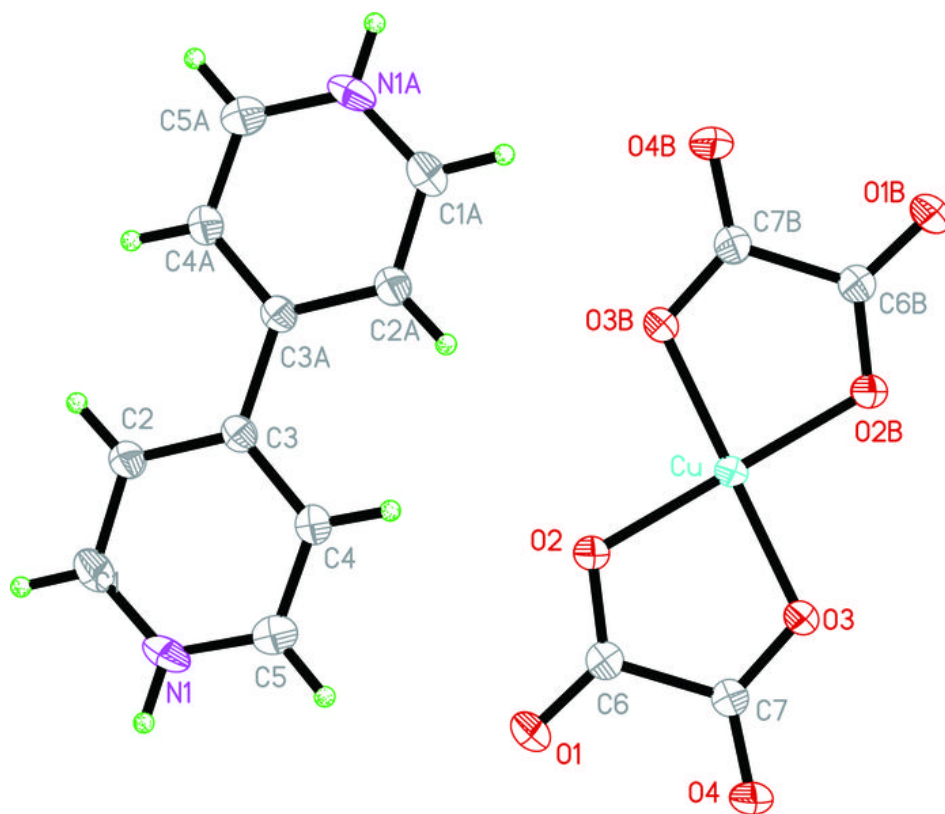


Fig. 2

