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Bis(2,2′-biimidazole-κ^2N,N')bis(2-bromofumarato-κO)copper(II)

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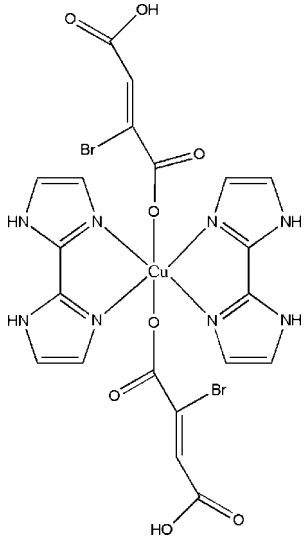
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.011 Å; R factor = 0.068; wR factor = 0.196; data-to-parameter ratio = 15.8.

In the title compound, $[Cu(C_4H_2BrO_4)_2(C_6H_6N_4)_2]$, the central Cu^{II} atom lies on an inversion center and is six-coordinated in an octahedral geometry by four N atoms from two chelating biimidazole molecules in the equatorial plane and two O atoms from two 2-bromofumarate ligands in the axial positions. O—H···O, N—H···O and C—H···O hydrogen bonds lead to a three-dimensional network.

Related literature

For related literature, see: Atencio *et al.* (2005); Carraza *et al.* (2003); Öhrström *et al.* (2001); Sang & Xu (2006); Tadokoro *et al.* (1999). For the synthesis and crystal structure of 2-bromofumaric acid, see: Fischer (2006).



Experimental

Crystal data

$[Cu(C_4H_2BrO_4)_2(C_6H_6N_4)_2]$
M_r = 719.77
Triclinic, $P\overline{1}$
a = 7.1650 (14) Å
b = 8.6458 (17) Å
c = 9.841 (2) Å
α = 83.13 (1)°
β = 84.21 (3)°
γ = 87.56 (2)°
V = 601.9 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 4.29 mm^{-1}
T = 295 (2) K
0.12 × 0.1 × 0.09 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.601, T_{max} = 0.685
5942 measured reflections
2717 independent reflections
1655 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.196
S = 1.06
2717 reflections
172 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N4	2.001 (5)	Cu—O4	2.627 (6)
Cu—N2	2.028 (5)		
N4—Cu—N2	81.9 (2)	N4^i—Cu—O4	92.7 (2)
N4^i—Cu—N2	98.1 (2)	N2—Cu—O4	88.9 (2)
N4—Cu—O4	87.3 (2)	N2—Cu—O4^i	91.1 (2)

Symmetry code: (i) $-x, -y, -z+2$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{ii}	0.86	1.90	2.756 (8)	174
N3—H4···O4^{ii}	0.86	1.85	2.672 (8)	159
O2—H8···O1^{iii}	0.85	1.90	2.743 (9)	172
C1—H2···O3^{iv}	0.93	2.55	3.433 (10)	159
C5—H5···O1^{v}	0.93	2.58	3.432 (10)	153
C6—H6···O2^{vi}	0.93	2.56	3.329 (10)	141

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2105).

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supporting information

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S1. Comment

Because of its various deprotonation modes (H_2biim, Hbiim$^-$, biim^{2-}), the 2,2′-biimidazole ligand exhibits rich coordination patterns with various metals such as Ag^I (Sang & Xu, 2006), Ni^{II} (Tadokoro *et al.*, 1999), Cu^{II}(Atencio *et al.*, 2005; Carraza *et al.*, 2003) and Co^{III}Öhrström *et al.*, 2001). We report here the crystal structure of a Cu^{II} complex with neutral 2,2′-biimidazole molecule and 2-bromofumarate anion as ligands.

As illustrated in Fig. 1, the Cu atom shows a distorted octahedral coordination geometry, formed by four N atoms from two 2,2′-biimidazole molecules and two O atoms from carboxylate groups offered by two 2-bromofumarate ligands at the axial positions. The asymmetric unit contains an H_2biim molecule and a 2-bromofumarate anion with a Cu^{II} atom lying on an inversion center. We can see that the lengths of Cu—N bonds [2.028 (5) and 2.001 (5) Å] are slightly asymmetric (Table 1). This behavior is similar to the reported Cu complex with H_2biim [2.036 (2) and 2.010 (2) Å] (Atencio *et al.*, 2005). Three types of strong hydrogen bonds are observed. The O—H···O hydrogen bonds are formed between two adjacent uncoordinated carboxylate groups. The N—H···O hydrogen bonds are formed between H_2biim and the neighboring coordinated carboxylate group. Weak C—H···O hydrogen bonds also exist in the structure (Table 2). The complex molecules are assembled into two-dimensional layers *via* O—H···O and N—H···O hydrogen bonds. These layers are further assembled through C—H···O hydrogen bonds into a three-dimensional supramolecular structure.

S2. Experimental

In a 50 ml two-neck bottle, the mixture of 2,2′-biimidazole (1.340 g, 10 mmol), 2-bromofumaric acid (0.195 g, 10 mmol) (Fischer, 2006), water (10 ml) and methanol (10 ml) was heated to 353 K, and then copper(II) chloride dihydrate (0.170 g, 10 mmol) was added. The suspension was stirred and kept at 353 K for 3 h. After cooling to room temperature, the solid was filtered off and the green solution was allowed to evaporate in air. After one day, block green crystals suitable for X-ray diffraction were formed.

S3. Refinement

H atoms on C and N atoms were positioned geometrically and refined as riding, with C—H = 0.93 Å, N—H = 0.86Å and U_{iso}(H) = 1.2U_{eq}(C,*N*). H atom attached to O atom was located in a difference Fourier map and fixed with U_{iso}(H) = 1.5U_{eq}(O).

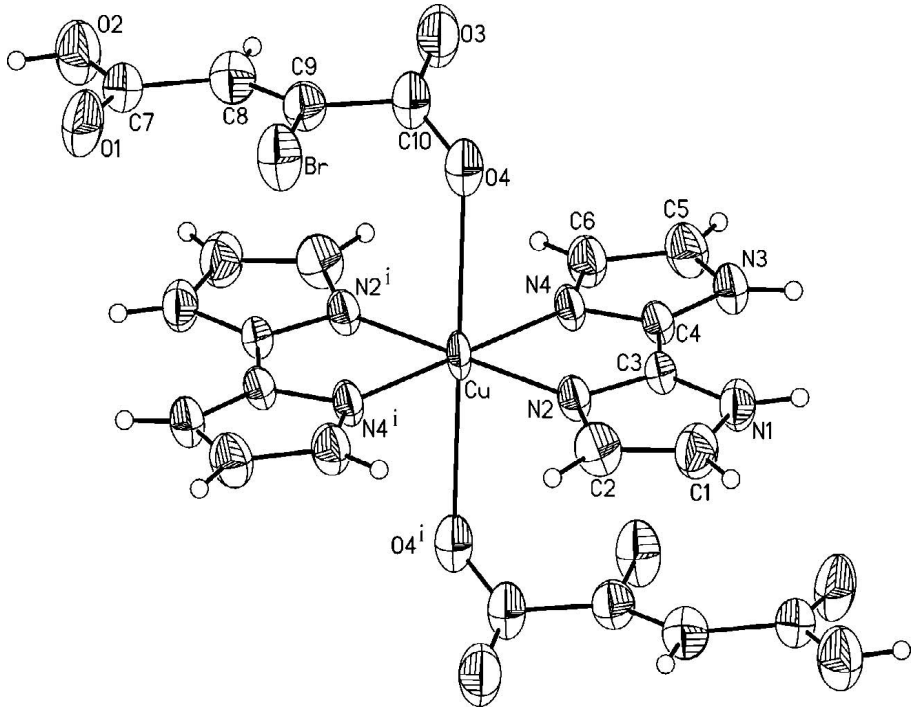

Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 45% probability level. [Symmetry code: (i) -*x*, -*y*, 2 - *z*.]

Bis(2,2′-biimidazole-κ^2N,N')bis(2-bromofumarato-κO)copper(II)

Crystal data

$[Cu(C_4H_2BrO_4)_2(C_6H_6N_4)_2]$
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Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.1650 (14) Å
b = 8.6458 (17) Å
c = 9.841 (2) Å
α = 83.13 (1)°
β = 84.21 (3)°
γ = 87.56 (2)°
V = 601.9 (2) Å^3
Z = 1
$F(000)$ = 355
D_x = 1.986 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2750 reflections
θ = 3.0–27.5°
μ = 4.29 mm^{-1}
T = 295 K
Platelet, green
0.12 × 0.1 × 0.09 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.601, T_{max} = 0.685
5942 measured reflections
2717 independent reflections
1655 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 27.5°, θ_{min} = 3.4°
h = −9→9
k = −11→11
l = −10→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.196$
$S = 1.06$
2717 reflections
172 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 0.1925P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.0000	0.0000	1.0000	0.0331 (3)
Br	−0.08553 (12)	0.49244 (10)	0.83673 (9)	0.0604 (4)
N1	0.3926 (8)	−0.0593 (7)	1.2738 (6)	0.0444 (14)
H1	0.4976	−0.1049	1.2915	0.053*
C1	0.2838 (12)	0.0336 (10)	1.3537 (8)	0.053 (2)
H2	0.3108	0.0628	1.4369	0.064*
O1	−0.3636 (9)	0.4989 (7)	0.6254 (6)	0.0682 (18)
N2	0.1405 (7)	0.0166 (6)	1.1664 (6)	0.0344 (12)
C2	0.1300 (11)	0.0765 (10)	1.2905 (8)	0.0497 (19)
H3	0.0302	0.1382	1.3246	0.060*
O2	−0.3039 (8)	0.3652 (7)	0.4506 (6)	0.0654 (17)
H8	−0.4087	0.4102	0.4343	0.098*
N3	0.4932 (8)	−0.2414 (7)	1.0080 (7)	0.0445 (15)
H4	0.5900	−0.2626	1.0522	0.053*
C3	0.3013 (9)	−0.0657 (7)	1.1606 (7)	0.0344 (14)
O3	0.2811 (8)	0.2094 (7)	0.6488 (6)	0.0643 (16)
N4	0.2205 (7)	−0.1400 (6)	0.9522 (6)	0.0334 (12)
C4	0.3456 (8)	−0.1495 (7)	1.0427 (7)	0.0336 (14)
O4	0.1940 (7)	0.2317 (7)	0.8670 (6)	0.0568 (12)
C5	0.4601 (10)	−0.2935 (9)	0.8885 (8)	0.0493 (19)
H5	0.5373	−0.3610	0.8399	0.059*
C6	0.2919 (10)	−0.2312 (9)	0.8536 (8)	0.0441 (18)
H6	0.2352	−0.2467	0.7755	0.053*
C7	−0.2662 (11)	0.4104 (9)	0.5622 (8)	0.0477 (18)
C8	−0.0839 (11)	0.3384 (9)	0.6025 (8)	0.0514 (19)
H7	−0.0230	0.2741	0.5416	0.062*
C9	0.0024 (10)	0.3520 (8)	0.7107 (8)	0.0459 (17)
C10	0.1763 (10)	0.2592 (10)	0.7433 (10)	0.0568 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0202 (6)	0.0442 (6)	0.0367 (6)	0.0114 (4)	−0.0126 (5)	−0.0077 (5)
Br	0.0523 (6)	0.0680 (6)	0.0663 (6)	0.0119 (4)	−0.0203 (5)	−0.0224 (5)
N1	0.032 (3)	0.058 (4)	0.046 (3)	0.006 (3)	−0.017 (3)	−0.005 (3)
C1	0.042 (5)	0.077 (5)	0.044 (4)	0.005 (4)	−0.021 (4)	−0.011 (4)
O1	0.058 (4)	0.093 (4)	0.060 (4)	0.020 (3)	−0.040 (3)	−0.015 (3)
N2	0.021 (3)	0.043 (3)	0.040 (3)	0.008 (2)	−0.006 (2)	−0.008 (3)
C2	0.045 (5)	0.067 (5)	0.042 (4)	0.002 (4)	−0.004 (4)	−0.025 (4)
O2	0.050 (4)	0.084 (4)	0.066 (4)	0.028 (3)	−0.018 (3)	−0.023 (3)
N3	0.023 (3)	0.051 (3)	0.059 (4)	0.010 (3)	−0.010 (3)	−0.003 (3)
C3	0.017 (3)	0.046 (3)	0.040 (4)	−0.001 (3)	−0.008 (3)	0.004 (3)
O3	0.044 (3)	0.082 (4)	0.068 (4)	0.020 (3)	−0.020 (3)	−0.007 (3)
N4	0.017 (3)	0.041 (3)	0.042 (3)	0.008 (2)	−0.007 (2)	−0.005 (2)
C4	0.017 (3)	0.040 (3)	0.045 (4)	0.002 (2)	−0.006 (3)	−0.003 (3)
O4	0.032 (2)	0.070 (3)	0.068 (3)	0.007 (2)	−0.022 (2)	0.004 (3)
C5	0.032 (4)	0.058 (4)	0.060 (5)	0.015 (3)	−0.006 (4)	−0.023 (4)
C6	0.030 (4)	0.056 (4)	0.048 (4)	0.013 (3)	−0.009 (3)	−0.013 (4)
C7	0.033 (4)	0.055 (4)	0.052 (5)	0.006 (3)	−0.009 (4)	0.008 (4)
C8	0.043 (5)	0.061 (5)	0.051 (5)	0.002 (4)	−0.011 (4)	−0.005 (4)
C9	0.036 (4)	0.049 (4)	0.053 (4)	−0.002 (3)	−0.010 (4)	0.000 (4)
C10	0.032 (2)	0.070 (3)	0.068 (3)	0.007 (2)	−0.022 (2)	0.004 (3)

Geometric parameters (Å, º)

Cu—N4	2.001 (5)	O2—H8	0.8512
Cu—N4^{i}	2.001 (5)	N3—C4	1.337 (8)
Cu—N2	2.028 (5)	N3—C5	1.354 (9)
Cu—N2^{i}	2.028 (5)	N3—H4	0.8600
Cu—O4	2.627 (6)	C3—C4	1.441 (9)
Cu—O4^{i}	2.627 (6)	O3—C10	1.242 (10)
Br—C9	1.883 (7)	N4—C4	1.319 (8)
N1—C3	1.355 (8)	N4—C6	1.369 (8)
N1—C1	1.358 (10)	O4—C10	1.230 (10)
N1—H1	0.8600	C5—C6	1.358 (10)
C1—C2	1.337 (11)	C5—H5	0.9300
C1—H2	0.9300	C6—H6	0.9300
O1—C7	1.200 (9)	C7—C8	1.492 (10)
N2—C3	1.329 (7)	C8—C9	1.304 (10)
N2—C2	1.377 (8)	C8—H7	0.9300
C2—H3	0.9300	C9—C10	1.494 (7)
O2—C7	1.266 (9)		
N4—Cu—N4^{i}	180.000 (1)	C5—N3—H4	126.8
N4—Cu—N2	81.9 (2)	N2—C3—N1	111.6 (6)
N4^{i}—Cu—N2	98.1 (2)	N2—C3—C4	117.0 (6)
N4—Cu—N2^{i}	98.1 (2)	N1—C3—C4	131.3 (6)

N4^{i}—Cu—N2^{i}	81.9 (2)	C4—N4—C6	105.7 (5)
N2—Cu—N2^{i}	180.000 (1)	C4—N4—Cu	112.8 (4)
N4—Cu—O4	87.3 (2)	C6—N4—Cu	141.5 (5)
N4^{i}—Cu—O4	92.7 (2)	N4—C4—N3	111.9 (6)
N2—Cu—O4	88.9 (2)	N4—C4—C3	116.9 (5)
N2^{i}—Cu—O4	91.1 (2)	N3—C4—C3	131.2 (6)
N4—Cu—O4^{i}	92.7 (2)	C10—O4—Cu	115.9 (5)
N4^{i}—Cu—O4^{i}	87.3 (2)	N3—C5—C6	107.7 (6)
N2—Cu—O4^{i}	91.1 (2)	N3—C5—H5	126.2
N2^{i}—Cu—O4^{i}	88.9 (2)	C6—C5—H5	126.1
O4—Cu—O4^{i}	180.00 (17)	C5—C6—N4	108.3 (6)
C3—N1—C1	106.0 (6)	C5—C6—H6	126.0
C3—N1—H1	127.0	N4—C6—H6	125.7
C1—N1—H1	127.0	O1—C7—O2	124.4 (7)
C2—C1—N1	107.8 (6)	O1—C7—C8	125.4 (7)
C2—C1—H2	125.7	O2—C7—C8	110.2 (7)
N1—C1—H2	126.5	C9—C8—C7	129.5 (8)
C3—N2—C2	104.6 (6)	C9—C8—H7	115.2
C3—N2—Cu	111.4 (4)	C7—C8—H7	115.3
C2—N2—Cu	143.8 (5)	C8—C9—C10	122.9 (7)
C1—C2—N2	109.9 (6)	C8—C9—Br	121.5 (6)
C1—C2—H3	125.5	C10—C9—Br	115.5 (6)
N2—C2—H3	124.6	O4—C10—O3	126.1 (7)
C7—O2—H8	105.0	O4—C10—C9	114.2 (8)
C4—N3—C5	106.3 (6)	O3—C10—C9	119.5 (8)
C4—N3—H4	126.9		

Symmetry code: (i) −*x*, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3^{ii}	0.86	1.90	2.756 (8)	174
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Symmetry codes: (ii) −*x*+1, −*y*, −*z*+2; (iii) −*x*−1, −*y*+1, −*z*+1; (iv) *x*, *y*, *z*+1; (v) *x*+1, *y*−1, *z*; (vi) −*x*, −*y*, −*z*+1.