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Bis[2-(2-hydroxy-3-methoxyphenyl)-benzimidazolium] tetrachloridocuprate(II) methanol disolvate

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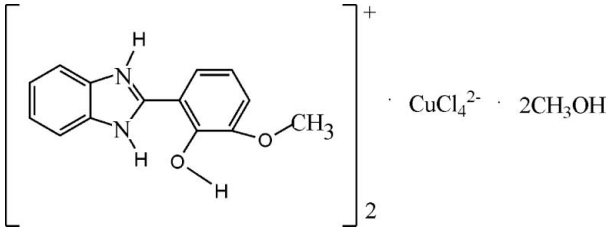
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.035; wR factor = 0.099; data-to-parameter ratio = 14.5.

In the title compound, $(C_{14}H_{13}N_2O_2)_2[CuCl_4]\cdot 2CH_4O$, the geometry of the $CuCl_4^{2-}$ ions (Cu site symmetry 2) is intermediate between tetrahedral and square-planar. The dihedral angle between the benzimidazole and benzene ring systems is 8.74(14)°. A network of N—H···O, N—H···Cl and O—H···Cl hydrogen bonds helps to consoldiate the structure. Aromatic π–π stacking interactions involving the benzimidazole ring system, with a centroid–centroid distance of 3.785 (3) Å, also occur.

Related literature

For background, see: Zhao *et al.* (2006).



Experimental

Crystal data

$(C_{14}H_{13}N_2O_2)_2[CuCl_4]\cdot 2CH_4O$
M_r = 751.95
Monoclinic, $C2/c$
a = 17.992 (2) Å
b = 9.9694 (16) Å
c = 19.849 (3) Å
β = 109.406 (2)°
V = 3358.1 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.02 mm^{-1}
T = 298 (2) K
0.55 × 0.32 × 0.29 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.605, T_{max} = 0.757
8468 measured reflections
2968 independent reflections
2273 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.099
S = 1.00
2968 reflections
204 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—Cu1	2.2297 (8)	Cu1—Cl2	2.2732 (8)
Cl1^{i}—Cu1—Cl1	99.99 (5)	Cl1—Cu1—Cl2	103.30 (3)
Cl1^{i}—Cu1—Cl2	128.83 (3)	Cl2—Cu1—Cl2^{i}	96.38 (5)

Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.09	2.634 (3)	120
N2—H2···O3	0.86	1.92	2.747 (3)	162
O3—H3···Cl2	0.82	2.44	3.245 (3)	168
N1—H1···Cl1^{ii}	0.86	2.55	3.298 (2)	147
O1—H1*A*···Cl2^{ii}	0.82	2.36	3.066 (2)	145

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: HB2652).

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Zhao, Y.-H., Su, Z.-M., Wang, Y., Hao, X.-R. & Shao, K.-Z. (2006). *Acta Cryst.* E**62**, m2361–m2362.

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supporting information

Acta Cryst. (2008). E**64**, m211 [https://doi.org/10.1107/S1600536807066214]

Bis[2-(2-hydroxy-3-methoxyphenyl)benzimidazolium] tetrachloridocuprate(II) methanol disolvate

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S1. Comment

2-(2-Hydroxyphenyl)benzimidazole complexes have potential applications in the fabrication of organic electroluminescent devices (*e.g.* Zhao *et al.*, 2006). In the title compound, (I), the organic species is protonated and does not bind to the metal ion (Fig. 1). The copper(II) ion (site symmetry 2) adopts a geometry intermediate between square planar and tetrahedral (Table 1).

In the crystal, a network of hydrogen bonds (Table 2) link the component species into chains (Fig. 2) The adjacent chains are cross-linked by π–π stacking interactions involving the two benzimidazole rings, with a centroid···centroid distance of 3.785 (3) Å.

S2. Experimental

To a solution of *o*-phenylenediamine (0.216 g, 2 mmol) in methanol (5 ml), *o*-vanillin (0.615 g, 4 mmol) was added. The mixture was refluxed for 1 h, then a solution of cupric chloride dihydrate (0.3408 g, 2 mmol) was added dropwise and the mixture stirred for another 3 h. Red blocks of (I) were grown by slow evaporation of the solvent after about two weeks.

S3. Refinement

All H atoms were placed in geometrically idealized positions (N—H = 0.86 Å, O—H = 0.82 Å, C—H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = 1.5U_{eq}(C_{methyl}, O) or 1.2U_{eq}(C).

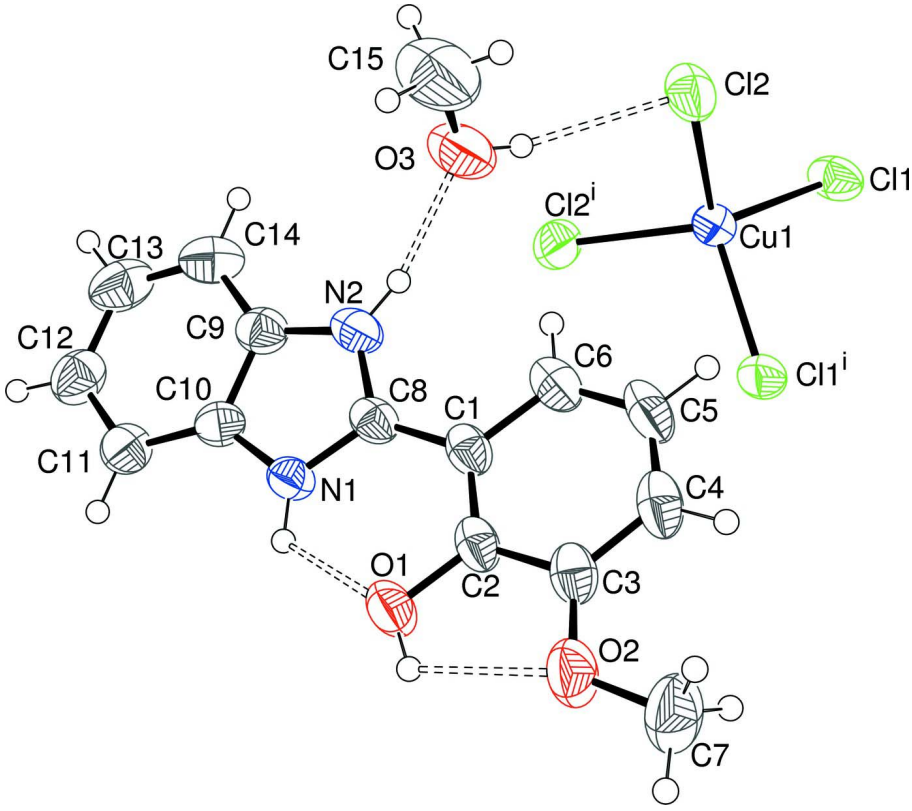

Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids for the non-hydrogen atoms. Symmetry code: (i) 1 - *x*, *y*, 1/2 - *z*.

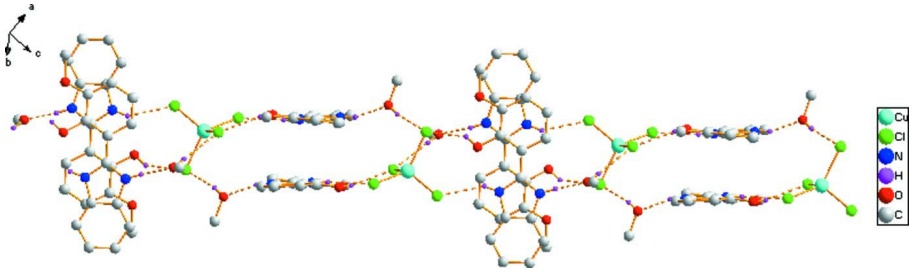

Figure 2

View of a hydrogen-bonded (dashed lines) chain in (I).

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Crystal data

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$M_r = 751.95$
Monoclinic, *C*2/*c*
$a = 17.992\ (2)$ Å
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$c = 19.849\ (3)$ Å
$\beta = 109.406\ (2)°$
$V = 3358.1\ (8)$ Å^3
$Z = 4$
$F(000) = 1548$
$D_x = 1.487$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3347 reflections
$\theta = 2.4–26.5°$
$\mu = 1.02$ mm^{-1}
$T = 298$ K
Block, red
0.55 × 0.32 × 0.29 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.605, T_{max} = 0.757
8468 measured reflections
2968 independent reflections
2273 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −17→21
k = −10→11
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.099
S = 1.00
2968 reflections
204 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 3.5756P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 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.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.43726 (4)	1.01765 (8)	0.16383 (4)	0.0528 (2)
Cu1	0.5000	0.87387 (5)	0.2500	0.03965 (16)
Cl2	0.40516 (4)	0.72185 (8)	0.24813 (5)	0.0618 (2)
N1	0.77757 (12)	0.5015 (2)	0.52156 (11)	0.0393 (5)
H1	0.8090	0.5266	0.5626	0.047*
N2	0.67538 (14)	0.4895 (3)	0.42615 (12)	0.0476 (6)
H2	0.6298	0.5056	0.3953	0.057*
O1	0.76890 (12)	0.6556 (2)	0.62645 (10)	0.0606 (6)
H1A	0.7874	0.7034	0.6617	0.091*
O2	0.70083 (13)	0.8504 (2)	0.67617 (11)	0.0651 (6)
O3	0.52158 (14)	0.4866 (3)	0.33663 (14)	0.0859 (9)
H3	0.4981	0.5543	0.3174	0.129*
C1	0.66881 (15)	0.6608 (3)	0.51403 (14)	0.0414 (7)
C2	0.70078 (15)	0.7102 (3)	0.58301 (15)	0.0425 (7)
C3	0.66309 (17)	0.8123 (3)	0.60765 (16)	0.0463 (7)
C4	0.59298 (18)	0.8638 (3)	0.56282 (18)	0.0533 (8)

H4	0.5665	0.9296	0.5792	0.064*
C5	0.56225 (17)	0.8174 (4)	0.49376 (18)	0.0585 (9)
H5	0.5159	0.8549	0.4633	0.070*
C6	0.59831 (17)	0.7175 (3)	0.46896 (16)	0.0524 (8)
H6	0.5762	0.6870	0.4223	0.063*
C7	0.6671 (2)	0.9575 (4)	0.7043 (2)	0.0764 (11)
H7A	0.6583	1.0334	0.6729	0.115*
H7B	0.7024	0.9823	0.7506	0.115*
H7C	0.6178	0.9287	0.7084	0.115*
C8	0.70637 (15)	0.5539 (3)	0.48807 (14)	0.0401 (6)
C9	0.72747 (17)	0.3928 (3)	0.41891 (15)	0.0459 (7)
C10	0.79306 (16)	0.4004 (3)	0.48014 (14)	0.0410 (7)
C11	0.85731 (17)	0.3171 (3)	0.49069 (16)	0.0489 (7)
H11	0.9014	0.3226	0.5317	0.059*
C12	0.85291 (19)	0.2254 (3)	0.43757 (18)	0.0586 (8)
H12	0.8948	0.1671	0.4428	0.070*
C13	0.7865 (2)	0.2184 (4)	0.37584 (19)	0.0683 (10)
H13	0.7858	0.1563	0.3407	0.082*
C14	0.7228 (2)	0.2999 (4)	0.36564 (17)	0.0635 (9)
H14	0.6785	0.2935	0.3250	0.076*
C15	0.4684 (3)	0.3940 (5)	0.3439 (3)	0.121 (2)
H15A	0.4913	0.3447	0.3875	0.182*
H15B	0.4547	0.3333	0.3041	0.182*
H15C	0.4218	0.4393	0.3453	0.182*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0484 (4)	0.0576 (5)	0.0422 (4)	−0.0070 (4)	0.0012 (3)	0.0115 (3)
Cu1	0.0358 (3)	0.0405 (3)	0.0399 (3)	0.000	0.00888 (19)	0.000
Cl2	0.0404 (4)	0.0512 (5)	0.0950 (6)	0.0002 (4)	0.0239 (4)	0.0185 (4)
N1	0.0310 (12)	0.0451 (14)	0.0391 (12)	−0.0005 (10)	0.0081 (9)	−0.0017 (10)
N2	0.0367 (13)	0.0549 (16)	0.0441 (13)	−0.0022 (12)	0.0038 (10)	0.0026 (12)
O1	0.0499 (12)	0.0718 (16)	0.0491 (11)	0.0258 (11)	0.0017 (9)	−0.0101 (11)
O2	0.0655 (14)	0.0698 (16)	0.0587 (13)	0.0287 (12)	0.0189 (11)	−0.0032 (12)
O3	0.0605 (15)	0.0776 (19)	0.0928 (18)	−0.0156 (14)	−0.0105 (13)	0.0301 (15)
C1	0.0307 (14)	0.0445 (17)	0.0493 (16)	0.0024 (13)	0.0137 (12)	0.0110 (13)
C2	0.0321 (14)	0.0440 (17)	0.0526 (16)	0.0068 (13)	0.0158 (12)	0.0106 (14)
C3	0.0418 (16)	0.0472 (18)	0.0556 (17)	0.0088 (14)	0.0239 (14)	0.0096 (14)
C4	0.0452 (17)	0.050 (2)	0.072 (2)	0.0142 (15)	0.0293 (16)	0.0159 (16)
C5	0.0334 (15)	0.064 (2)	0.074 (2)	0.0134 (16)	0.0128 (15)	0.0193 (18)
C6	0.0396 (16)	0.059 (2)	0.0531 (17)	0.0054 (15)	0.0085 (13)	0.0098 (15)
C7	0.092 (3)	0.072 (3)	0.074 (2)	0.027 (2)	0.038 (2)	−0.003 (2)
C8	0.0306 (14)	0.0449 (17)	0.0442 (15)	−0.0038 (13)	0.0114 (12)	0.0079 (13)
C9	0.0422 (16)	0.0481 (18)	0.0471 (16)	−0.0071 (14)	0.0142 (13)	0.0013 (14)
C10	0.0385 (15)	0.0423 (17)	0.0436 (15)	−0.0071 (13)	0.0154 (12)	−0.0010 (13)
C11	0.0428 (16)	0.0501 (19)	0.0564 (17)	−0.0013 (15)	0.0200 (13)	−0.0040 (15)
C12	0.057 (2)	0.052 (2)	0.073 (2)	−0.0023 (16)	0.0303 (17)	−0.0101 (17)

C13	0.074 (2)	0.066 (2)	0.070 (2)	−0.013 (2)	0.0302 (19)	−0.0246 (19)
C14	0.060 (2)	0.074 (3)	0.0518 (18)	−0.0150 (19)	0.0126 (16)	−0.0142 (18)
C15	0.082 (3)	0.110 (4)	0.149 (4)	−0.029 (3)	0.009 (3)	0.055 (3)

Geometric parameters (Å, º)

Cl1—Cu1	2.2297 (8)	C4—C5	1.377 (5)
Cu1—Cl1^{i}	2.2297 (8)	C4—H4	0.9300
Cu1—Cl2	2.2732 (8)	C5—C6	1.366 (4)
Cu1—Cl2^{i}	2.2732 (8)	C5—H5	0.9300
N1—C8	1.338 (3)	C6—H6	0.9300
N1—C10	1.386 (3)	C7—H7A	0.9600
N1—H1	0.8600	C7—H7B	0.9600
N2—C8	1.334 (4)	C7—H7C	0.9600
N2—C9	1.385 (4)	C9—C10	1.386 (4)
N2—H2	0.8600	C9—C14	1.388 (4)
O1—C2	1.356 (3)	C10—C11	1.382 (4)
O1—H1A	0.8200	C11—C12	1.377 (4)
O2—C3	1.357 (4)	C11—H11	0.9300
O2—C7	1.431 (4)	C12—C13	1.400 (5)
O3—C15	1.372 (5)	C12—H12	0.9300
O3—H3	0.8200	C13—C14	1.364 (5)
C1—C2	1.387 (4)	C13—H13	0.9300
C1—C6	1.405 (4)	C14—H14	0.9300
C1—C8	1.445 (4)	C15—H15A	0.9600
C2—C3	1.398 (4)	C15—H15B	0.9600
C3—C4	1.378 (4)	C15—H15C	0.9600
Cl1^{i}—Cu1—Cl1	99.99 (5)	O2—C7—H7A	109.5
Cl1^{i}—Cu1—Cl2	128.83 (3)	O2—C7—H7B	109.5
Cl1—Cu1—Cl2	103.30 (3)	H7A—C7—H7B	109.5
Cl1^{i}—Cu1—Cl2^{i}	103.30 (3)	O2—C7—H7C	109.5
Cl1—Cu1—Cl2^{i}	128.83 (3)	H7A—C7—H7C	109.5
Cl2—Cu1—Cl2^{i}	96.38 (5)	H7B—C7—H7C	109.5
C8—N1—C10	109.7 (2)	N2—C8—N1	107.9 (2)
C8—N1—H1	125.1	N2—C8—C1	125.6 (2)
C10—N1—H1	125.1	N1—C8—C1	126.5 (2)
C8—N2—C9	109.9 (2)	N2—C9—C10	106.2 (3)
C8—N2—H2	125.0	N2—C9—C14	132.3 (3)
C9—N2—H2	125.0	C10—C9—C14	121.5 (3)
C2—O1—H1A	109.5	C11—C10—N1	132.1 (3)
C3—O2—C7	117.7 (2)	C11—C10—C9	121.7 (3)
C15—O3—H3	109.5	N1—C10—C9	106.2 (2)
C2—C1—C6	118.4 (3)	C12—C11—C10	116.8 (3)
C2—C1—C8	121.6 (2)	C12—C11—H11	121.6
C6—C1—C8	120.0 (3)	C10—C11—H11	121.6
O1—C2—C1	118.4 (2)	C11—C12—C13	121.2 (3)
O1—C2—C3	120.7 (3)	C11—C12—H12	119.4

C1—C2—C3	120.9 (2)	C13—C12—H12	119.4
O2—C3—C4	126.1 (3)	C14—C13—C12	122.1 (3)
O2—C3—C2	114.5 (2)	C14—C13—H13	119.0
C4—C3—C2	119.4 (3)	C12—C13—H13	119.0
C5—C4—C3	119.8 (3)	C13—C14—C9	116.7 (3)
C5—C4—H4	120.1	C13—C14—H14	121.6
C3—C4—H4	120.1	C9—C14—H14	121.6
C6—C5—C4	121.5 (3)	O3—C15—H15A	109.5
C6—C5—H5	119.3	O3—C15—H15B	109.5
C4—C5—H5	119.3	H15A—C15—H15B	109.5
C5—C6—C1	120.0 (3)	O3—C15—H15C	109.5
C5—C6—H6	120.0	H15A—C15—H15C	109.5
C1—C6—H6	120.0	H15B—C15—H15C	109.5

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	2.09	2.634 (3)	120
N2—H2···O3	0.86	1.92	2.747 (3)	162
O3—H3···Cl2	0.82	2.44	3.245 (3)	168
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O1—H1*A*···Cl2^{ii}	0.82	2.36	3.066 (2)	145

Symmetry code: (ii) $x+1/2, -y+3/2, z+1/2$.