

Dibromotetrakis(4-methylimidazole)copper(II) dihydrate

Christian Näther,* Mario Wriedt
and Inke Jeß

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

Correspondence e-mail:
cnaether@ac.uni-kiel.de

Key indicators

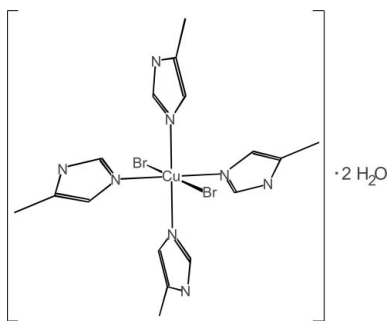
Single-crystal X-ray study
 $T = 293\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 H-atom completeness 99%
 Disorder in solvent or counterion
 R factor = 0.043
 wR factor = 0.111
 Data-to-parameter ratio = 20.8

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

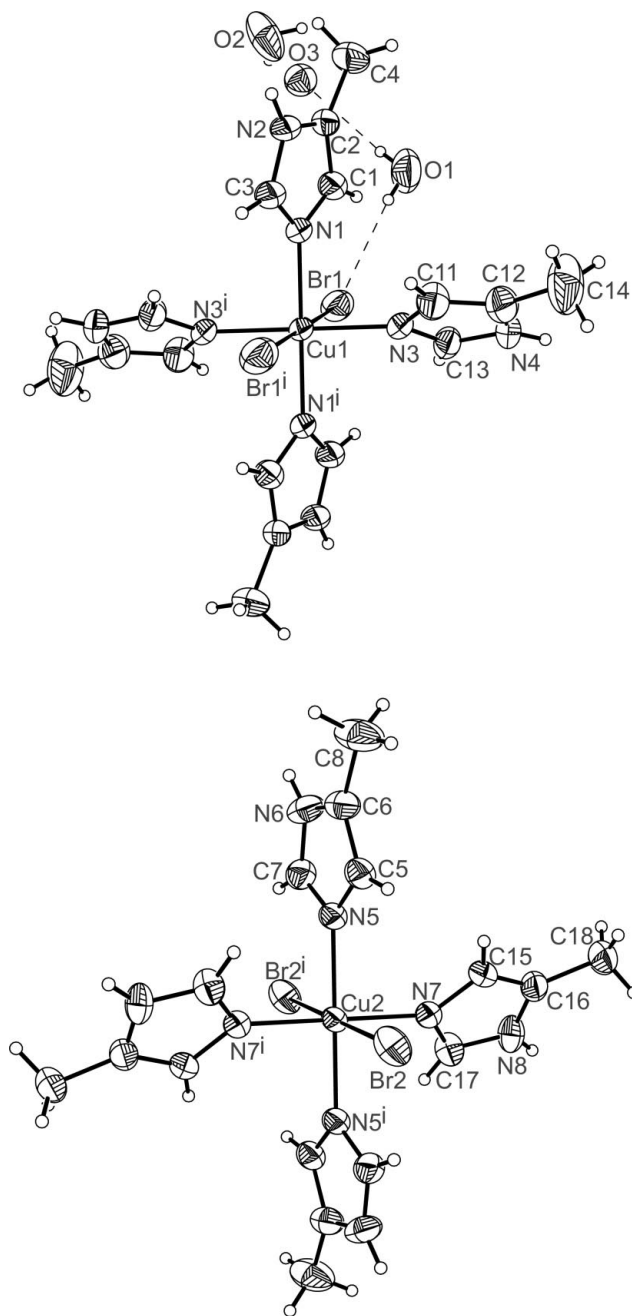
In the structure of the title compound, $[\text{CuBr}_2(\text{C}_4\text{H}_6\text{N}_2)_4]\cdot 2\text{H}_2\text{O}$, the Cu^{II} atoms are surrounded by four 4-methylimidazole ligands within a slightly distorted square plane. The coordination sphere is completed by two contacts to bromide ligands which are elongated due to Jahn–Teller distortion. The coordination polyhedra around the Cu^{II} cations can be described as strongly distorted octahedral. There are two crystallographically independent half-complexes in the asymmetric unit, in which the Cu^{II} cations are located on centres of inversion; the two crystallographically independent 4-methylimidazole ligands, the bromide anions and the water molecules occupy general positions. The complexes are connected *via* $\text{N}-\text{H}\cdots\text{Br}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding.

Comment

In the crystal structure of the title compound, (I), the Cu^{II} atoms are coordinated by four N atoms of 4-methylimidazole ligands, forming a slightly distorted square plane. The $\text{Cu}-\text{N}$ distances of 2.003 (3), 2.014 (3), 1.993 (3) and 2.029 (3) Å are comparable to those in other 4-methylimidazole–copper(II) complexes, such as dichlorotetrakis(4-methylimidazole)-copper(II) and dibromotetrakis(4-methylimidazole)copper(II) (Näther *et al.*, 2002*a,b*), and tetrakis(4-methylimidazolyl)bis(perchlorato-*O*)copper(II) (Su *et al.*, 1992), as well as tetrakis(4-methylimidazol-1-yl)bis(cyanamidonitrate)copper(II) (Kohout *et al.*, 1999). The coordination sphere of the Cu^{II} atoms is completed by two longer contacts to two symmetry-equivalent Br atoms located above and below the tetragonal plane. The $\text{Cu}-\text{Br}$ distances of 3.2851 (8) Å (Cu1–Br1) and 3.1957 (9) Å (Cu2–Br2) are strongly elongated due to Jahn–Teller distortion and the coordination polyhedra around the Cu^{II} atoms can be described as strongly distorted octahedral.



(I)


Figure 1

The crystal structure of the title compound, with labelling and displacement ellipsoids drawn at the 50% probability level [symmetry codes: (i) $-x+1, -y+1, -z+1$]. Hydrogen bonds are indicated by dashed lines.

The asymmetric unit contains two crystallographically independent half-complexes in which the 4-methylimidazole ligands, the water molecules and the Br atoms occupy general positions, whereas the Cu^{II} atoms are located on centres of inversion. In contrast to the non-hydrated compound dibromotetrakis(4-methylimidazole)copper(II) (Näther *et al.*, 2002*b*), the title compound contains additional water molecules and crystallizes as the dihydrate. Therefore, this

compound represents a pseudo-polymorphic modification of the former compound. There are short N—H···Br and O—H···Br distances between the NH H atoms of the 4-methylimidazole ligand, as well as the OH H atoms of the water molecules, and the Br atoms. The distances and angles of these interactions indicate hydrogen bonding. The water molecules are additionally connected to the 4-methylimidazole ligand *via* N—H···O hydrogen bonding. From all of these intermolecular interactions, a three-dimensional hydrogen-bonded network results.

Experimental

The title compound was prepared by the reaction of 335.1 mg (4 mmol) 4-methylimidazole and 223.4 mg (1 mmol) copper(II) bromide in 5 ml water. The reaction mixture was stirred over a period of 3 d, filtered and was washed with dimethyl ether. The precipitate consists of a blue crystalline powder and a few blue single crystals suitable for X-ray structure determination.

Crystal data

[CuBr₂(C₄H₆N₂)₄]₂·2H₂O
M_r = 587.82
 Triclinic, *P* $\bar{1}$
a = 9.891 (2) Å
b = 10.613 (2) Å
c = 13.063 (3) Å
 α = 94.854 (13)°
 β = 100.87 (2)°
 γ = 116.933 (13)°
V = 1177.8 (4) Å³

Z = 2
D_x = 1.658 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 78 reflections
 θ = 10–18°
 μ = 4.35 mm⁻¹
T = 293 (2) K
 Block, blue
 0.14 × 0.08 × 0.06 mm

Data collection

AED-II four-circle diffractometer
 ω - θ scans
 Absorption correction: numerical
 (*X-SHAPE*; Stoe & Cie, 1998)
T_{min} = 0.687, *T_{max}* = 0.881
 6010 measured reflections
 5686 independent reflections
 3712 reflections with *I* > 2σ(*I*)

R_{int} = 0.037
 θ_{\max} = 28.0°
h = 0 → 13
k = -14 → 12
l = -17 → 16
 4 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR(*F*²) = 0.111
S = 1.01
 5686 reflections
 274 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.8939P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max}$ = 1.34 e Å⁻³
 $\Delta\rho_{\min}$ = -1.22 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0052 (8)

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	2.003 (3)	Cu2—N7	1.993 (3)
Cu1—N3	2.014 (3)	Cu2—N5	2.029 (3)
N1 ⁱ —Cu1—N3	92.93 (12)	N7—Cu2—N5	91.15 (12)
N1—Cu1—N3	87.07 (12)	N7 ⁱⁱ —Cu2—N5	88.85 (12)

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

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2N \cdots Br2 ⁱ	0.86	2.60	3.443 (3)	168
N4—H4N \cdots O1 ⁱⁱ	0.86	2.02	2.863 (5)	165
N6—H6N \cdots Br1 ⁱⁱⁱ	0.86	2.70	3.410 (4)	141
N8—H8N \cdots O2 ^{iv}	0.86	1.96	2.803 (6)	167
N8—H8N \cdots O3 ^{iv}	0.86	2.09	2.883 (17)	154
O1—H1O1 \cdots O3	0.82	2.41	3.044 (18)	135
O1—H1O1 \cdots Br2 ^v	0.82	3.02	3.773 (4)	154
O1—H2O1 \cdots Br1	0.82	2.58	3.371 (4)	163
O2—H1O2 \cdots Br2 ^v	0.82	2.62	3.430 (5)	169
O2—H2O2 \cdots Br2	0.82	2.49	3.255 (5)	157

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

The aromatic H atoms were positioned with idealized geometry (C—H = 0.93 Å and N—H = 0.86 Å). The positions of the methyl H atoms were idealized (C—H = 0.96 Å), then the methyl groups were refined as rigid groups allowed to rotate but not tip. The water H atoms were located in a difference map and the bond lengths were set to ideal values (O—H = 0.82 Å). All H atoms were refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$, $1.5U_{\text{eq}}(\text{O})$, $1.2U_{\text{eq}}(\text{C}_{\text{methylene}})$ or $1.2U_{\text{eq}}(\text{N})$], using a riding model. One water O atom is disordered over two positions and these were refined with a split model (O2 and O3) and site-occupation factors of

0.8 for O2 and 0.2 for O3. The H atoms attached to O3 were ignored. Atom O3 was refined with an isotropic displacement parameter.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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