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Diaqua(diethylenetriamine-κ^3N)(perchlorato-κO)copper(II) hydrogenmaleate

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The title compound, $[Cu(ClO_4)(dien)(H_2O)_2](Hmal)$, where dien is diethylenetriamine ($C_4H_{13}N_3$) and Hmal ($C_4H_3O_4$) is the hydrogenmaleate anion, contains discrete $[Cu(dien)(H_2O)_2]^{2+}$ cations and ClO_4^- and $Hmal^-$ anions. The cation has a square-pyramidal geometry for the primary dien and aqua ligands, with the perchlorate weakly coordinated in a sixth position opposite the apex. The cation and anion lie on crystallographic mirror planes. For the cation, the mirror plane bisects the molecule and runs through two O atoms of the water molecules and the central N atom of the dien ligand. The mirror plane bisects the perchlorate through Cl and two O atoms. A mirror plane is perpendicular to the plane of the Hmal anion, bisecting the central C=C double bond and containing the hydroxyl H atom.

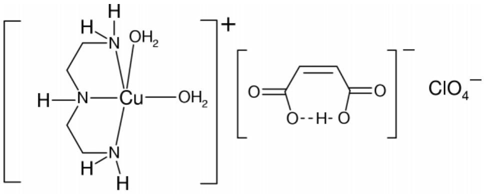
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.115
Data-to-parameter ratio = 11.3

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

Comment

Recently, we have carried out studies on the possible use of $[Cu(dien)]^{2+}$ as a tecton in the supramolecular synthesis of Cu^{II} coordination polymers. It is reasonable to suggest that in aqueous solution the $[Cu(dien)]^{2+}$ cation is present as $[Cu(dien)(H_2O)_2]^{2+}$. To the best of our knowledge, in the solid state, this cation has only been reported twice (Mikloš *et al.*, 2001; Valdés-Martínez *et al.*, 1993). In this paper, we report the structure of the title compound, (I), which contains the above-mentioned cation and perchlorate and hydrogenmaleate anions, the perchlorate being weakly coordinated to Cu.



(I)

The geometry of the $[Cu(dien)(H_2O)_2]^{2+}$ cation is square-pyramidal, with the three N atoms of the dien and a water molecule, O2, forming the basal plane. A water molecule in the apical position, O1, is involved in a longer Cu—O bond distance than the other water, O2 (Hathaway, 1987; see Table 1). The perchlorate is only weakly coordinated, in a sixth site opposite the apical water molecule The Hmal anion is essentially planar with a maximum deviation of 0.003 (3) Å for atom C3. The C3—O3 and C3—O4 bond distances indicate electron delocalization.

In the crystal structure, cations are linked through N—H$\cdots$O$_{water}$ hydrogen bonds to form extended chains in the **c** direction (Fig. 2). In addition, cations and anions are linked through O$_{water}$—H$\cdots$O hydrogen bonds to form layers

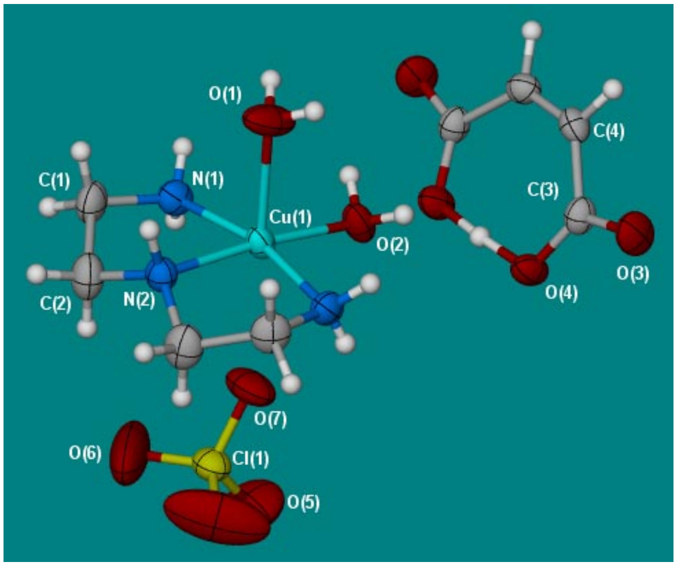


Figure 1
The asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level.

parallel to the *bc* plane (Fig. 3). Hydrogen-bond geometries are listed in Table 2.

Experimental

1.0 mmol of $CuClO_4 \cdot 6H_2O$ was dissolved in the minimum amount of distilled H_2O, and 1.0 mmol of dien was added to the solution. A solution of 1.0 mmol of maleic acid in distilled water was added to the Cu–dien solution and the mixture was stirred for 15 min and left to slowly evaporate until blue crystals were obtained.

Crystal data

$[Cu(ClO_4)(C_4H_{17}N_4)(H_2O)_2](C_4H_3O_4)$
$M_r = 417.26$
Monoclinic, $C2/m$
$a = 24.975$ (2) Å
$b = 9.714$ (1) Å
$c = 6.5213$ (4) Å
$\beta = 95.327$ (1)°
$V = 1575.3$ (2) Å^3
$Z = 4$
$D_x = 1.759$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3981 reflections
$\theta = 2.3$–24.9°
$\mu = 1.61$ mm^{-1}
$T = 293$ (2) K
Prism, dark blue
0.36 × 0.23 × 0.13 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: analytical (*SHELXTL*; Bruker, 1999)
$T_{min} = 0.610$, $T_{max} = 0.814$
6480 measured reflections
1476 independent reflections
1303 reflections with $I > 2\sigma(I)$’
$R_{int} = 0.049$
$\theta_{max} = 25.0°$
$h = -29 \rightarrow 29$
$k = -11 \rightarrow 11$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.115$
$S = 1.07$
1476 reflections
131 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 1.3338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

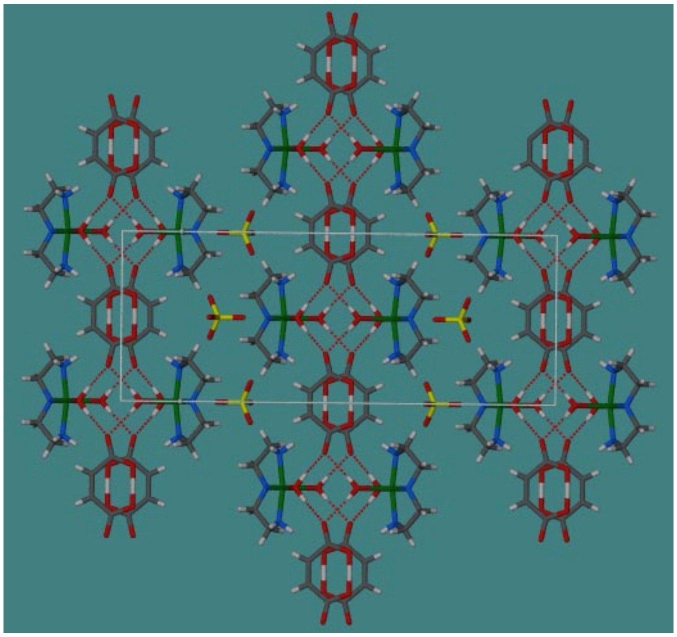


Figure 2
The packing of (I), viewed along the *c* axis. Hydrogen bonds are indicated by dashed lines.

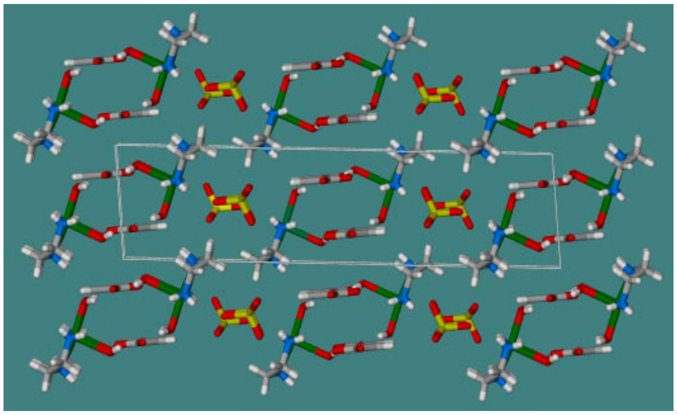


Figure 3
The packing of (I), viewed along the *c* axes. Hydrogen bonds are indicated by dashed lines.

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.994 (4)	Cu1—O7	2.711 (4)
Cu1—N1	2.007 (3)	O3—C3	1.231 (4)
Cu1—O2	2.018 (4)	O4—C3	1.267 (4)
Cu1—O1	2.275 (4)		
N2—Cu1—N1	84.95 (9)	N2—Cu1—O7	91.36 (15)
N1^i—Cu1—N1	166.83 (19)	N1—Cu1—O7	85.91 (10)
N2—Cu1—O2	173.36 (16)	O2—Cu1—O7	82.00 (15)
N1—Cu1—O2	94.53 (9)	O1—Cu1—O7	179.98 (16)
N2—Cu1—O1	88.66 (19)	O3—C3—O4	122.8 (3)
N1—Cu1—O1	94.09 (10)	O3—C3—C4	117.1 (3)
O2—Cu1—O1	97.97 (18)	O4—C3—C4	120.1 (3)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2$C\cdots$O2^{ii}	0.97 (5)	2.38 (6)	3.309 (6)	161 (4)
N1—H1$D\cdots$O4	0.86 (4)	2.38 (4)	3.160 (4)	151 (3)
O2—H2$A\cdots$O3^{iii}	0.88 (4)	1.83 (4)	2.696 (3)	168 (4)
O1—H1$A\cdots$O3^{i}	0.79 (5)	2.03 (5)	2.809 (4)	167 (5)

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

All H atoms bonded to C were found in a difference Fourier map and refined using a riding model, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). H atoms bonded to N and O were refined, giving N—H distances of 0.69 (4)-0.97 (5)Å and O—H distances of 0.79 (5)/ 0.88 (4) Å (for O1 and O2), respectively. Atom H4 is on a mirror plane with an O—H distance of 1.209 (4) Å. $U_{\rm iso}$ of the N- and O-bonded H atoms were constrained as for the C-bonded H atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *X-Seed* (Barbour, 2001); software used to prepare material for publication: *SHELXTL* (Bruker, 1999).

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