Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Aquabis(9-hydroxyfluorene-9-carboxylato)(methanol)copper(II) methanol disolvate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.057
wR factor = 0.154
Data-to-parameter ratio = 17.1

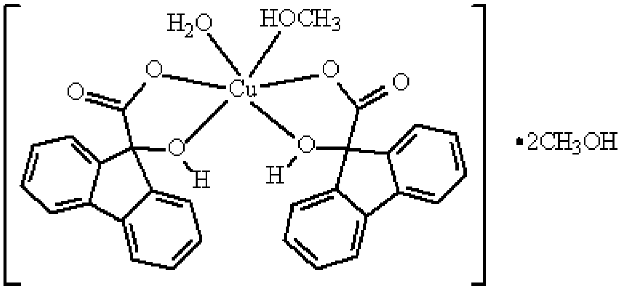
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 October 2004
Accepted 21 October 2004
Online 30 October 2004

In the title mononuclear complex, $[Cu(C_{14}H_9O_3)_2(CH_4O)(H_2O)]\cdot 2CH_3OH$, the Cu^{II} atom has an elongated octahedral coordination environment, defined by two hydroxyl and two carboxylate O atoms from two bidentate 9-hydroxyfluorene-9-carboxylate ligands, and one water and one methanol molecule in *cis* positions. A supramolecular chain structure is constructed *via* hydrogen-bonding interactions.

Comment

There has been considerable interest in α-hydroxylate derivatives of fluorene-9-carboxylic acid in structural chemistry and biochemistry (Feng & Liu, 2002; Liu & Wang, 1996; Bkouche, 1994). 9-Hydroxyfluorene-9-carboxylic acid, which could bind to a metal centre through its carboxyl and/or hydroxyl O atoms, is a potentially multidentate ligand. Liu and co-workers have reported some Cu^{II} complexes prepared from 9-hydroxyfluorene-9-carboxylic acid and *N*-heterocyclic amine ligands, with mononuclear (Zheng *et al.*, 1999; Feng & Liu, 2002), binuclear (Liu & Yu, 1992; Yu *et al.*, 1996) and two-dimensional layer (Liu, 1992) structures. In this paper, we report the crystal structure of the title compound, (I).



(I)

As shown in Fig. 1, the crystal structure of (I) consists of a mononuclear Cu^{II} complex and two solvent methanol molecules. Atom Cu1 is bonded by hydroxyl atoms O3 and O6 and carboxyl atoms O1 and O4 from two bidentate 9-hydroxyfluorene-9-carboxylate ligands, and by water atom O1*W* and methanol atom O7, displaying an elongated octahedral configuration. The equatorial plane is defined by atoms O1/O1*W*/O4/O6, while the axial coordination sites are occupied by atoms O3 and O7, the Cu—O7 bond length [2.519 (2) Å] being the longest of the Cu—O distances (Table 1).

The hydroxyl groups of the 9-hydroxyfluorene-9-carboxylate ligands in (I) are not deprotonated, while in the previously reported mononuclear Cu^{II} complex $[Cu(C_{14}H_8O_3)(C_5H_{13}NO)(H_2O)]\cdot 0.5H_2O$, (II), the hydroxyl group of this

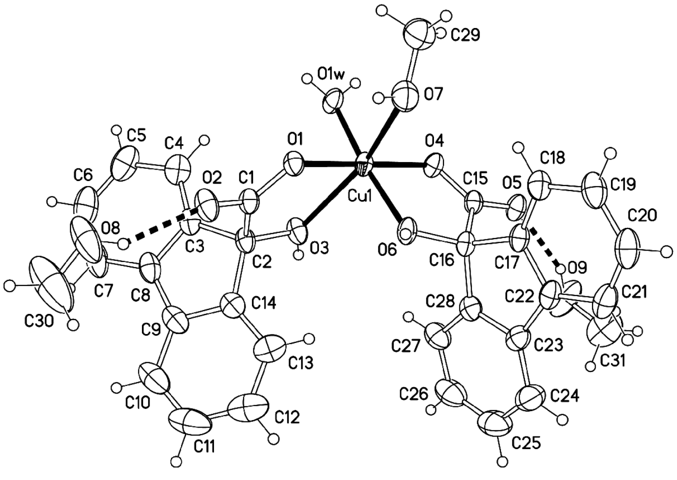


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

ligand is deprotonated (Feng & Liu, 2002). In (II), the coordination geometry around the Cu^{II} atom is distorted square pyramidal. The basal plane consists of bidentate ligands, a 9-oxofluorene-9-carboxylate dianion and *N*,*N*-dimethyl-2-propanolamine, while the axial coordination site is occupied by a water molecule, the Cu—O(oxo) bond length being 1.906 (2) Å.

The C1—O1 [1.283 (4) Å] and C15—O4 [1.284 (3) Å] distances in (I) are slightly longer than the C1—O2 [1.229 (3) Å] and C15—O5 [1.233 (3) Å] distances, in agreement with the greater double-bond character of the latter bonds. These indicate that the carboxyl groups of the 9-hydroxyfluorene-9-carboxylate ligands adopt a monodentate coordination mode to the Cu^{II} ion. Each of the five-membered chelate rings formed by the 9-hydroxyfluorene-9-carboxylate ligands is approximately planar. The dihedral angle between the two five-membered chelate rings is 88.9 (3)°, and that between the two fluorene planes is 40.7 (8)°.

The hydroxyl and carboxylate groups and the methanol and water molecules form an extensive hydrogen-bonding network (Table 2), consolidating the crystal structure of (I) and leading to a hydrogen-bonded supramolecular chain structure along the *b* axis (Fig. 2).

Experimental

The ligand 9-hydroxyfluorene-9-carboxylic acid was prepared following the literature method of Zheng *et al.* (1999). A solution of copper(II) acetate monohydrate (0.20 g, 1 mmol) was prepared in a methanol solution (20 ml) containing 9-hydroxyfluorene-9-carboxylic acid (0.44 g, 2 mmol) and the pH was adjusted to 6 with 0.2 *M* NaOH solution. The resulting solution was stirred for 30 min at room temperature and then filtered. Blue crystals of (I) were isolated from the solution at room temperature over several days (yield 51%). Elemental analysis, calculated: C 59.28, H 5.13%; found: C 59.48, H 5.19%.

Crystal data

$[Cu(C_{14}H_9O_3)_2(CH_4O)(H_2O)]\cdot 2CH_4O$
$M_r = 628.12$
Monoclinic, $P2_1/n$
$a = 13.592$ (3) Å
$b = 7.5178$ (15) Å
$c = 29.233$ (6) Å
$\beta = 90.69$ (3)°
$V = 2986.9$ (11) Å^3
$Z = 4$

$D_x = 1.397$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 670 reflections
$\theta = 3.1$–27.5°
$\mu = 0.79$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.39 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID area-detector diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.749$, $T_{max} = 0.871$
26 886 measured reflections

6772 independent reflections
5332 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -9 \rightarrow 9$
$l = -37 \rightarrow 37$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.154$
$S = 1.05$
6772 reflections
397 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2 + 2.4818P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.950 (2)	Cu1—O1*W*	1.943 (2)
Cu1—O3	2.355 (2)	O1—C1	1.283 (4)
Cu1—O4	1.943 (2)	O2—C1	1.229 (3)
Cu1—O6	1.982 (2)	O4—C15	1.284 (3)
Cu1—O7	2.519 (2)	O5—C15	1.233 (3)
O1—Cu1—O3	73.65 (8)	O4—Cu1—O1*W*	90.84 (8)
O1—Cu1—O6	95.20 (8)	O6—Cu1—O3	89.99 (9)
O1—Cu1—O7	79.20 (8)	O6—Cu1—O7	84.97 (9)
O3—Cu1—O7	151.78 (9)	O1*W*—Cu1—O1	92.41 (9)
O4—Cu1—O1	175.43 (8)	O1*W*—Cu1—O3	92.93 (10)
O4—Cu1—O3	109.39 (8)	O1*W*—Cu1—O6	172.34 (8)
O4—Cu1—O6	81.51 (8)	O1*W*—Cu1—O7	95.68 (10)
O4—Cu1—O7	97.31 (9)		
O1—C1—C2—O3	7.7 (4)	O4—C15—C16—O6	4.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H32···O8^{i}	0.85 (3)	1.83 (3)	2.671 (4)	176 (4)
O6—H33···O9^{ii}	0.84 (3)	1.73 (3)	2.567 (3)	176 (4)
O7—H34···O5^{ii}	0.82	2.41	3.175 (4)	156
O8—H35···O2	0.82	1.97	2.693 (4)	147
O9—H36···O5	0.82	2.02	2.797 (4)	157
O1*W*—H1*W*2···O1^{iii}	0.84 (3)	1.91 (3)	2.737 (3)	169 (4)
O1*W*—H1*W*1···O4^{iv}	0.84 (3)	1.87 (3)	2.699 (3)	170 (4)

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

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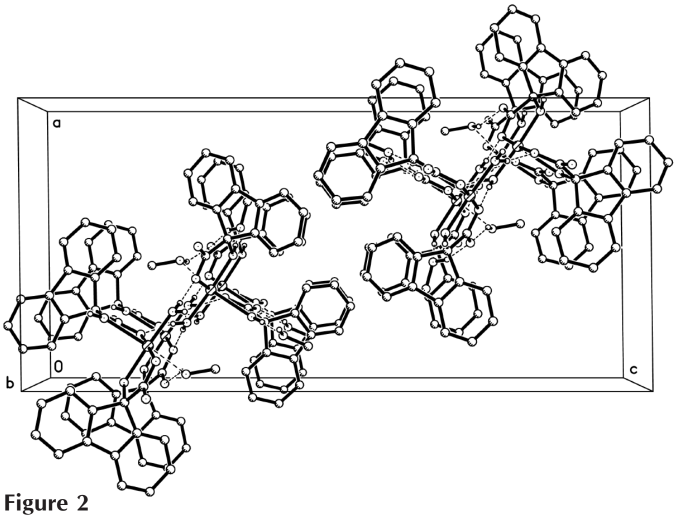

Figure 2
A packing diagram for (I). Dashed lines indicate hydrogen bonds. H atoms have been omitted.

The H atoms of the hydroxy groups and water molecule were located in a difference Fourier map and refined with the O—H distance restrained to 0.85 (1) Å and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). Methanol H atoms bonded to atoms O7, O8 and O9 were placed in idealized positions consistent with a difference synthesis and treated as riding, with O—H = 0.82 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). The remaining H atoms were placed in calculated positions and were allowed to ride on their parent C atoms, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for the aromatic H atoms, and with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for the methyl H atoms.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

The authors thank the National Natural Science Foundation of China (grant No. 20101003), Heilongjiang Province Natural Science Foundation (grant No. B0007), the Outstanding Teacher Foundation of Heilongjiang Province (grant No. 1054G036) and Heilongjiang University for supporting this work.

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