Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(9-hydroxyfluorene-9-carboxylato-κ^2O,O')-bis(3-hydroxypyridine-κN)copper(II) methanol disolvate

Shan Gao,[a] Li-Hua Huo[a] and Seik Weng Ng[b]*

[a]College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Received 28 September 2005
Accepted 30 September 2005
Online 5 October 2005

Key indicators

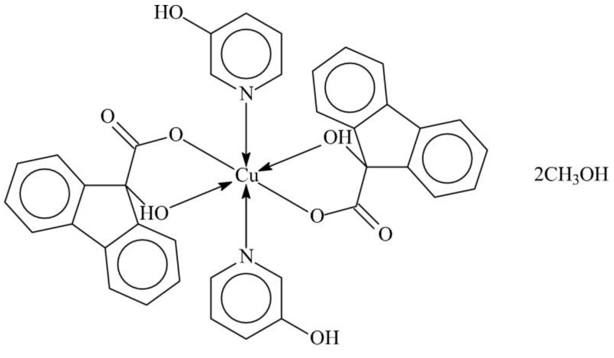
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.033
wR factor = 0.101
Data-to-parameter ratio = 13.8

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

In the title compound, $[Cu(C_{14}H_9O_3)_2(C_5H_5NO)_2]\cdot 2CH_3OH$, the Cu atom (site symmetry $\overline{1}$) is chelated by two 9-hydroxyfluorene-9-carboxylate ligands. Two N-bound 3-hydroxypyridine molecules, which are disordered over two adjacent positions, complete the coordination of the distorted CuO_4N_2 octahedron. Various O—H⋯O hydrogen bonds link the metal-bearing unit and the methanol solvent molecules into a linear chain structure.

Comment

Copper(II) acetate reacts with two molar equivalents of sodium 9-hydroxyfluorene-9-carboxylate, Na(hfc), Na$(C_{14}H_9O_3)$, in the presence of imidazole, $C_3H_4N_2$, to yield the dinuclear adduct $[Cu_2(C_{14}H_8O_3)_2(C_3H_4N_2)(H_2O)_2]\cdot CH_3OH$ (Huo *et al.*, 2004). In the resulting compound, the hfc hydroxy group is deprotonated and the resulting $(C_{14}H_8O_3)$ species bears a charge of −2.



(I)

The title compound, (I), arose when 3-hydroxypyridine was used as the *N*-heterocycle in place of imidazole. The synthesis did not lead to the deprotonation of the hydroxy group of hfc; instead the reaction yielded the mononuclear complex as a methanol disolvate, (I) (Fig. 1). The Cu ion occupies a special position with $\overline{1}$ site symmetry; the four O atoms of the two chelating hfc$^-$ ligands constitute a CuO_4 rhombus. Above and below this array, the N atoms of the nitrogen heterocycles complete the distorted CuO_4N_2 octahedron (Table 1), with the Cu1—O3 bonds in axial sites.

Various O—H⋯O hydrogen bonds (Table 2) link the mononuclear species and the solvent molecules into an extended chain.

Experimental

Copper diacetate monohydrate (0.20 g, 1 mmol) was dissolved in methanol (20 ml) and 9-hydroxyfluorene-9-carboxylic acid (0.44 g, 2 mmol) and 3-hydroxypyridine (0.19 g, 2 mmol) were added sequentially. Drops of 0.1 *M* sodium hydroxide were then added until the pH of the mixture was about 7. The solution was filtered; blue crystals of (I) separated from solution after several days. Elemental analysis calculated (found) for $C_{40}H_{36}CuN_2O_{10}$: C 62.54 (62.59), H 4.72 (4.69), N 3.65% (3.62%).

Crystal data

$[Cu(C_{14}H_9O_3)_2(C_5H_5NO)_2]\cdot 2CH_4O$
$M_r = 768.25$
Monoclinic, $P2_1/n$
$a = 14.877$ (3) Å
$b = 7.872$ (2) Å
$c = 16.527$ (3) Å
$\beta = 112.04$ (3)°
$V = 1794.2$ (6) Å^3
$Z = 2$
$D_x = 1.422$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14783 reflections
$\theta = 3.0$–27.5°
$\mu = 0.67$ mm^{-1}
$T = 295$ (2) K
Block, blue
0.38 × 0.26 × 0.18 mm

Data collection

Rigaku RAXIS-RAPID IP diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.684$, $T_{max} = 0.889$
16937 measured reflections
4101 independent reflections
3706 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = -19 \rightarrow 19$
$k = -10 \rightarrow 10$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.101$
$S = 1.05$
4101 reflections
298 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.3683P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.973 (1)	Cu1—O3	2.295 (1)
Cu1—N1	2.028 (1)		
O1—Cu1—O3	75.74 (4)	O1—Cu1—N1^i	89.01 (5)
O1—Cu1—O3^i	104.26 (4)	O3—Cu1—N1	92.00 (5)
O1—Cu1—N1	90.99 (5)	O3—Cu1—N1^i	88.00 (5)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3*o*···O5	0.82	2.02	2.677 (2)	137
O5—H5*o*···O2^{ii}	0.82	1.96	2.773 (2)	170
O4—H4*o*···O2^{ii}	0.82	1.91	2.702 (4)	162
O4'—H4'*o*···O1^{ii}	0.82	2.04	2.838 (6)	166

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

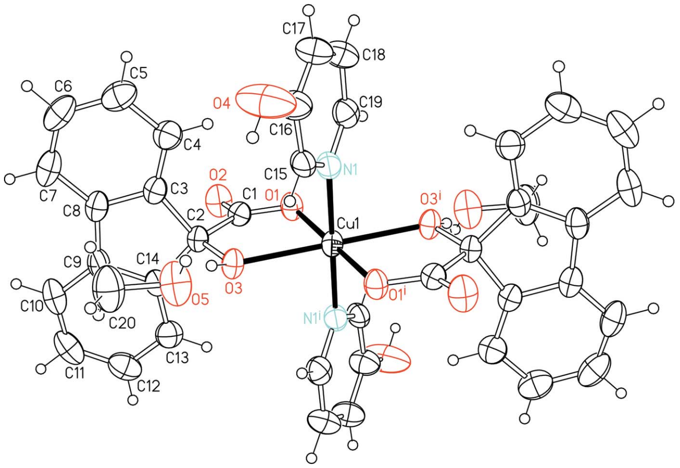


Figure 1
View of (I), showing 50% displacement ellipsoids (H atoms are drawn as spheres of arbitrary radius). Only the major orientations of the disordered 3-hydroxypyridine ligands are shown. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

The 3-hydropyridine ligand is disordered over two side-by-side positions with site occupancies of 0.66 (1):0.34 (1). Various geometrical restraints (N—C = 1.35 (1) Å, C—C = 1.39 (1) Å and C—O = the same within 0.01 Å) were used to stabilize the refinement; additionally, the displacement parameters of atoms C15, C19 and N1 were restrained to approximate isotropic behavior. The C- and O-bound H atoms were positioned geometrically, and were included in the refinement in the riding-model approximation (aromatic C—H = 0.93 Å, aliphatic C—H = 0.96 Å and O—H = 0.82 Å), with $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier). sp^3 Hybridization was assumed for the —OH group of the carboxylate, as well as for the methanol molecule; for the latter species, the hydroxyl and methyl groups were rotated to fit the electron density. The hydroxyl group of the nitrogen heterocycle was assumed to be coplanar, with the pyridyl ring in an sp^2-hybridization mode.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: difference Fourier, with Cu at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund for Remarkable Teachers of Heilongjiang Province (No. 1054 G036) and the University of Malaya for supporting this study.

References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Huo, L.-H., Gan, S., Zhao, H. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m1747–m1749.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, TX 77382-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Acta Cryst. (2005). E**61**, m2192–m2193 Gao *et al.* • $[Cu(C_{14}H_9O_3)_2(C_5H_5NO)_2]\cdot 2CH_4O$ **m2193**