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Bis(μ-9-oxidofluorene-9-carboxylato-$\kappa^3O,O':O$)-bis[aqua(1*H*-imidazole-κN^3)copper(II)] methanol solvate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.034
wR factor = 0.086
Data-to-parameter ratio = 15.2

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

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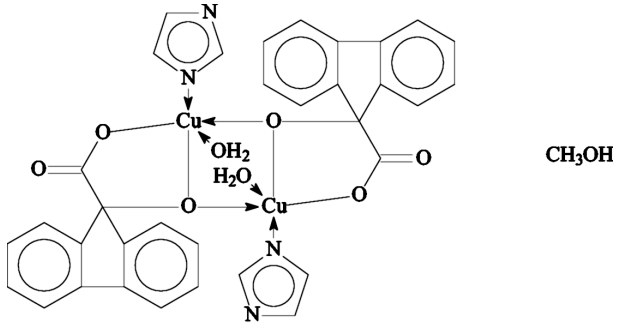
The title compound, $[Cu_2(C_{14}H_8O_3)_2(C_3H_4N_2)_2(H_2O)_2]\cdot CH_4O$, consists of oxo-bridged dinuclear complex molecules together with methanol solvent molecules. The dimers have twofold rotation symmetry. Cu has square-pyramidal coordination, with water in the apical site. The methanol molecule is disordered over a twofold rotation axis.

Comment

A number of adducts of copper(II) 9-hydroxyfluorene-9-carboxylate complexes have been synthesized; interestingly, the compounds pack with the crystal structure with solvent molecules that fill up the voids in the crystal structure. Among the solvates are, for example, the pyridine adduct, which crystallizes with methanol (Zheng *et al.*, 1999), the quinoline adduct, which crystallizes with DMF (Yu *et al.*, 1996), the 4,4′-bipyridine adduct, which crystallizes with DMF (Liu, 1992), and the phenanthroline adduct, which crystallizes with water (Liu & Liu, 1992). The 1-(dimethylamino)propan-2-ol adduct is also a hydrate (Feng & Liu, 2002).



(I)

In the title compound, (I), the 9-hydroxyfluorene-9-carboxylate dianion chelates to the metal atom in the imidazole adduct, which exists as a dinuclear entity arising from the interaction of the deprotonated hydroxy O atom of each monomeric unit with the Cu atom of the other across a twofold rotation axis. The square-pyramidal geometry of the Cu atom is completed by the water ligand at the apical position (Fig. 1). The compound crystallizes as a methanol solvate; the solvate is disordered as it lies on a twofold axis.

Experimental

A methanol solution of copper diacetate monohydrate (0.20 g, 1 mmol) was mixed with an ethanol solution of 9-hydroxyfluorene-9-carboxylic acid (0.44 g, 2 mmol) and an ethanol solution of imidazole (0.04 g, 1 mmol). Drops of 0.1 *M* sodium hydroxide were added to

give an approximate pH of 7. Blue crystals separated from the filtered solution after several days. As the elemental composition and thermal analysis were not consistent with the X-ray formulation, the crystal selected for the measurements is probably not representative of the bulk sample.

Crystal data

$[Cu_2(C_{14}H_8O_3)_2(C_3H_4N_2)_2(H_2O)_2]\cdot CH_4O$	D_x = 1.533 Mg m^{-3}
M_r = 779.73	Mo $K\alpha$ radiation
Orthorhombic, *Aba*2	Cell parameters from 14470 reflections
a = 17.228 (3) Å	θ = 3.0–29.7°
b = 14.464 (3) Å	μ = 1.32 mm^{-1}
c = 13.556 (3) Å	T = 295 (2) K
V = 3377.9 (12) Å^3	Prism, blue
Z = 4	0.37 × 0.26 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	3785 independent reflections
ω scans	3610 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	R_{int} = 0.024
T_{min} = 0.513, T_{max} = 0.788	θ_{max} = 27.5°
14628 measured reflections	$h = -22 \rightarrow 22$
	$k = -18 \rightarrow 18$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.3152P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.086	$\Delta\rho_{max}$ = 1.04 e Å^{-3}
S = 1.12	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
3785 reflections	Absolute structure: Flack (1983), from 1767 Friedel pairs
249 parameters	Flack parameter = 0.36 (1)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.929 (1)	Cu1—N1	1.961 (2)
Cu1—O3^{i}	1.943 (2)	Cu1—O1*w*	2.380 (3)
Cu1—O1	1.951 (2)		
O1—Cu1—O3	83.1 (1)	O3—Cu1—O1*w*	96.1 (1)
O1—Cu1—O3^{i}	159.3 (1)	O3—Cu1—N1	168.5 (1)
O1—Cu1—O1*w*	97.6 (1)	O3^{i}—Cu1—O1*w*	92.5 (1)
O1—Cu1—N1	95.4 (1)	O3^{i}—Cu1—N1	101.6 (1)
O3—Cu1—O3^{i}	77.9 (1)	O1*w*—Cu1—N1	95.4 (1)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*w*1···O4	0.85 (1)	2.11 (3)	2.892 (7)	153 (5)
N2—H2*n*···O2^{ii}	0.85 (1)	1.95 (1)	2.792 (3)	170 (3)

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

Carbon-bound H atoms were placed in calculated positions [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for the aromatic H atom; C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms], and were included in the refinement in the riding-model approximation. The amino and water H atoms were located and refined with distance restraints of N—H = O—H = 0.85 (1) Å and H···H = 1.39 (1) Å; the displacement parameters were fixed at 1.2U_{eq} of the parent atoms. The methanol solvent molecule was allowed to refine as two disordered components related by twofold rotation symmetry, without symmetry constraints on the individual components. The C—O distance was restrained to 1.50 (1) Å. The structure is an inversion twin, the twin component refining to 0.36 (1). The final difference Fourier map had a peak in a solvent-accessible void that is 2.8 Å from atom O11, but attempts to model the electron density led to a worse refinement.

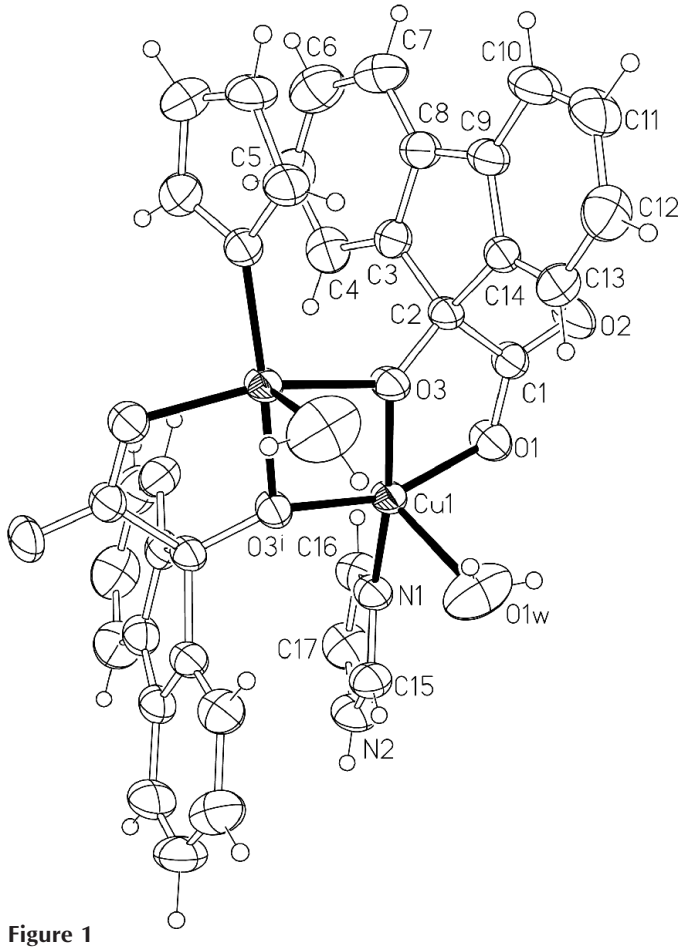


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I) displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The methanol solvent molecule is not shown.

Data collection: *RAPID-AUTO* (Rigaku, 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.

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