
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, hydrogen bonds and complete geometry have been deposited with the IUCr (Reference: NA1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dimeric Copper(II) Complex of an α-Hydroxylated Acid: [$Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2.2C_3H_7NO.2H_2O$

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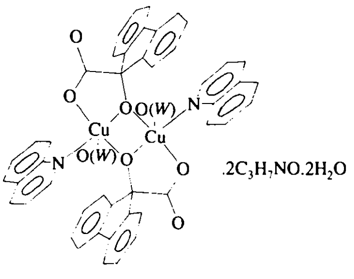
Abstract

The structure of bis[μ-(9-hydroxy-1:2κ^2O)-9-fluorenecarboxylato(2−)]-1κO;2κO-bis[aqua(quinoline-κN)copper(II)] bis(dimethylformamide) dihydrate has been determined by single-crystal X-ray diffraction. The binuclear Cu^{II} unit comprises a pair of Cu atoms linked by two hydroxy O-atom bridges. The coordination polyhedron around each Cu atom is a distorted square pyramid, the basal plane consisting of one N atom from the quinoline ligand, one carboxy O atom and two bridging O atoms from two α-hydroxylated acid ligands, while the axial coordination site is occupied by an O atom of the coordinated water molecule with a Cu—O bond length of 2.424 (4) Å.

Comment

There are two structure types in copper complexes of α-hydroxylated acid: mononuclear structures (Prout *et al.*, 1968; Bkouche-Waksman, 1994) and binuclear structures with a Cu_2O_2 core (Liu, 1992; Liu & Yu, 1992). This work is a part of our study on copper complexes of α-hydroxylated acid. The title compound, (I), is composed of one [$Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2$ binuclear unit, two DMF solvent molecules and two uncoordinated water molecules. The molecular configuration is shown in Fig. 1; atoms labelled *a* are related by the centre of inversion to those listed in Table 1. Therefore, the binuclear unit with a Cu_2O_2 core possesses a centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) with a Cu(1)···Cu(1*a*) distance of 3.007 (4) Å and Cu(1)—O(1)—Cu(1*a*) angle of 103.1 (1)°. The Cu atom is coordinated by two bridging hydroxy O atoms [O(1) and O(1*a*)] of two acid ligands, one carboxy O atom [O(3)], one N atom [N(1)] of the quinoline ligand, and one O atom [O(5)] of one coordinated water molecule, to form a distorted square-pyramidal polyhedron; the Cu(1) atom is shifted 0.183 Å out of the basal plane of O_3N towards the axial atom, O(5). The most distorted bond angles are 76.9 (1), 166.6 (2) and 159.2 (1)° in the square pyramid; the Cu—O(1*a*) bond of 1.936 (3) Å is 0.03 Å longer than Cu—O(1) [1.904 (3) Å]. These structural characteristics are seen in some other copper complexes of α-hydroxylated acids (Liu, 1992; Liu & Yu, 1992).



(I)

The axial Cu(1)—O(5)(water) bond length of 2.424 (4) Å is in good agreement with the usual Cu–

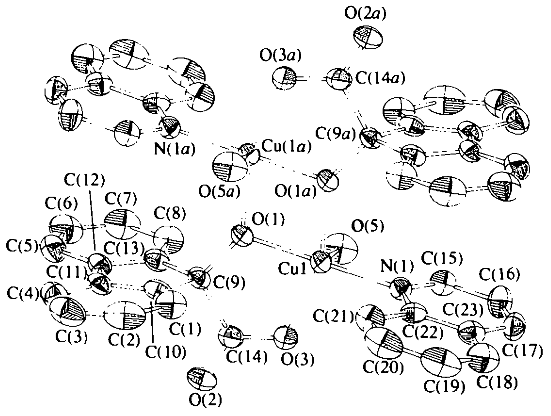


Fig. 1. A view of the binuclear unit [$Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2$ showing the atom numbering and 30% probability displacement ellipsoids.

axial-O(water) distances in five-coordinate copper complexes (Allen, Kennard & Taylor, 1983; Tahirov, Lu, Shu & Chung, 1994; Bkouche-Waksman, 1994). The coordination effect is seen in a shortening of the C(14)—O(3) bond distance [1.272 (5) Å] compared with the corresponding bond length [1.313 (5) Å] in methyl 9-hydroxy-9-fluorenecarboxylate (Liu, Huang & Wang, 1988).

There are some hydrogen bonds between the OH group of the coordinated water molecule and the carboxy O atom of the DMF molecule and the uncoordinated water molecule and between coordinated and uncoordinated water molecules, as shown in Table 3 and Fig. 2.

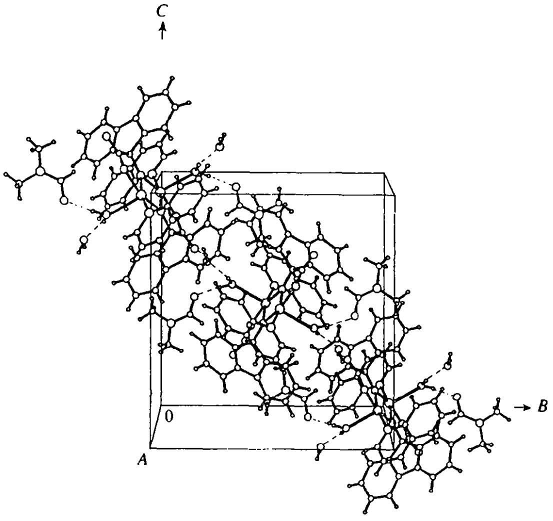


Fig. 2. Packing diagram viewed down the *a* axis showing the hydrogen bonding. Cu atoms are shown as large circles, other non-H atoms as medium circles, H atoms as small circles. Note the binuclear unit in the centre of the cell.

Experimental

Copper nitrate (10 mmol) dissolved in ethyl alcohol reacted with $C_{12}H_8C(OH)COOH$ (10 mmol) in ethyl alcohol under stirring. A light green precipitate formed. The solid was isolated by filtration and then dissolved in quinoline to give crystals of the title complex.

Crystal data

$[Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2.2C_3H_7NO.2H_2O$
$M_r = 1502.09$
Monoclinic
$P2_1/n$
$a = 11.073\ (3)$ Å
$b = 14.640\ (3)$ Å
$c = 14.979\ (2)$ Å
$\beta = 100.36\ (2)°$
$V = 2389\ (2)$ Å^3
$Z = 2$
$D_x = 1.46$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 13–15°$
$\mu = 0.999$ mm^{-1}
$T = 296$ K
Prism
0.52 × 0.25 × 0.20 mm
Dark green

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.56$, $T_{max} = 0.82$
5188 measured reflections
4928 independent reflections

2727 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.055$
$\theta_{max} = 26.1°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 150 reflections
intensity decay: 2.8%

Refinement

Refinement on F
$R = 0.0437$
$wR = 0.0530$
$S = 1.25$
2727 reflections
316 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu(1)	0.36968 (5)	0.46861 (4)	0.49493 (4)	2.37 (2)
O(1)	0.5032 (2)	0.4598 (2)	0.4311 (2)	2.5 (1)
O(2)	0.3098 (3)	0.3288 (3)	0.2673 (2)	4.1 (2)
O(3)	0.2810 (3)	0.4049 (2)	0.3894 (2)	3.1 (1)
O(4)	0.2999 (5)	0.1548 (3)	0.5105 (3)	6.9 (3)
O(5)	0.3983 (3)	0.3243 (2)	0.5752 (2)	4.0 (2)
O(6)	0.5768 (5)	0.2177 (4)	0.6894 (4)	9.8 (3)
N(1)	0.2289 (3)	0.5071 (3)	0.5498 (2)	2.2 (1)
N(2)	0.3506 (4)	0.0580 (4)	0.4058 (3)	4.7 (2)
C(1)	0.4365 (4)	0.5571 (3)	0.2415 (4)	3.4 (2)
C(2)	0.4587 (5)	0.5984 (4)	0.1616 (4)	4.5 (3)
C(3)	0.5347 (6)	0.5568 (4)	0.1097 (4)	4.5 (3)
C(4)	0.5922 (5)	0.4759 (4)	0.1359 (3)	3.5 (2)
C(5)	0.7112 (4)	0.2925 (4)	0.2404 (3)	3.5 (2)
C(6)	0.7463 (5)	0.2206 (4)	0.2981 (4)	4.2 (3)
C(7)	0.6968 (5)	0.2082 (4)	0.3750 (4)	4.0 (3)
C(8)	0.6085 (5)	0.2678 (4)	0.3959 (3)	3.4 (2)
C(9)	0.4804 (4)	0.4154 (3)	0.3470 (3)	2.2 (2)
C(10)	0.4922 (4)	0.4751 (3)	0.2661 (3)	2.5 (2)
C(11)	0.5721 (4)	0.4354 (3)	0.2152 (3)	2.5 (2)
C(12)	0.6223 (4)	0.3520 (3)	0.2608 (3)	2.5 (2)
C(13)	0.5717 (4)	0.3392 (3)	0.3385 (3)	2.3 (2)
C(14)	0.3460 (4)	0.3783 (3)	0.3325 (3)	2.5 (2)
C(15)	0.2022 (4)	0.4622 (3)	0.6204 (3)	2.7 (2)
C(16)	0.1031 (4)	0.4850 (4)	0.6615 (3)	3.4 (2)
C(17)	0.0305 (4)	0.5554 (4)	0.6306 (3)	3.1 (2)
C(18)	−0.0155 (5)	0.6818 (4)	0.5209 (4)	3.8 (3)
C(19)	0.0131 (6)	0.7287 (4)	0.4515 (4)	4.4 (3)
C(20)	0.1134 (6)	0.7040 (4)	0.4111 (4)	4.4 (3)
C(21)	0.1840 (5)	0.6309 (4)	0.4428 (3)	3.4 (2)
C(22)	0.1578 (4)	0.5803 (3)	0.5168 (3)	2.3 (2)
C(23)	0.0560 (4)	0.6065 (3)	0.5572 (3)	2.7 (2)
C(24)	0.3940 (6)	0.0466 (6)	0.3215 (5)	7.0 (4)
C(25)	0.3185 (7)	−0.0229 (5)	0.4500 (5)	6.7 (4)
C(26)	0.3359 (6)	0.1394 (5)	0.4401 (5)	5.4 (3)

Table 2. *Selected geometric parameters (Å, °)*

Cu(1)—O(1)	1.904 (3)	N(2)—C(24)	1.439 (7)
Cu(1)—O(1^i)	1.936 (3)	N(2)—C(25)	1.433 (8)
Cu(1)—O(3)	1.942 (3)	N(2)—C(26)	1.320 (8)
Cu(1)—N(1)	1.972 (3)	C(9)—C(10)	1.519 (6)

Cu(1)—O(5)	2.424 (4)	C(9)—C(13)	1.525 (6)
O(1)—C(9)	1.400 (5)	C(9)—C(14)	1.562 (6)
O(2)—C(14)	1.224 (5)	C(10)—C(11)	1.395 (6)
O(3)—C(14)	1.272 (5)	C(11)—C(12)	1.459 (7)
O(4)—C(26)	1.214 (7)	C(12)—C(13)	1.392 (6)
N(1)—C(15)	1.322 (6)	Cu(1)···Cu(1^i)	3.007 (4)
N(1)—C(22)	1.367 (5)		
O(1)—Cu(1)—O(1^i)	76.9 (1)	C(26)—N(2)—C(24)	122.0 (6)
O(1)—Cu(1)—O(3)	83.3 (1)	O(1)—C(9)—C(10)	115.0 (4)
O(1)—Cu(1)—N(1)	166.6 (2)	O(1)—C(9)—C(14)	107.4 (3)
O(1^i)—Cu(1)—O(3)	159.2 (1)	C(10)—C(9)—C(13)	101.6 (3)
O(1^i)—Cu(1)—N(1)	98.9 (1)	C(1)—C(10)—C(11)	121.2 (4)
O(3)—Cu(1)—N(1)	98.9 (1)	C(11)—C(10)—C(9)	110.5 (4)
O(5)—Cu(1)—O(1)	98.4 (1)	C(4)—C(11)—C(10)	120.5 (5)
O(5)—Cu(1)—O(1^i)	99.9 (1)	C(10)—C(11)—C(12)	108.6 (4)
O(5)—Cu(1)—O(3)	89.3 (1)	C(5)—C(12)—C(13)	120.5 (5)
O(5)—Cu(1)—N(1)	94.9 (1)	C(5)—C(12)—C(11)	130.3 (4)
Cu(1)—O(1)—Cu(1^i)	103.1 (1)	C(8)—C(13)—C(12)	120.5 (4)
C(9)—O(1)—Cu(1)	116.9 (2)	C(8)—C(13)—C(9)	129.3 (4)
C(9)—O(1)—Cu(1^i)	139.6 (2)	O(2)—C(14)—O(3)	124.9 (4)
C(14)—O(3)—Cu(1)	115.3 (3)	O(3)—C(14)—C(9)	116.1 (4)
C(15)—N(1)—C(22)	118.8 (4)	N(1)—C(15)—C(16)	122.8 (4)
C(15)—N(1)—Cu(1)	119.8 (3)	N(1)—C(22)—C(21)	120.8 (4)
C(22)—N(1)—Cu(1)	121.3 (3)	O(4)—C(26)—N(2)	126.1 (6)
C(26)—N(2)—C(25)	120.6 (5)		

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O(5)—H(23)···O(4)	1.885	2.811 (6)	167.1
O(6)—H(26)···O(2^i)	1.813	2.720 (6)	160.4
O(5)—H(24)···O(6)	1.996	2.838 (6)	146.8

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

The data were corrected for Lorentz–polarization effects. Difference Fourier maps revealed maxima in positions consistent with the expected locations of all H atoms. In the final round of calculations, the H atoms of the quinoline and α-hydroxylated acid ligands were positioned on geometrical grounds. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1989).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethylammonium Tris(pyridine-2-thiolato-*S*,*N*)cobalt(II), $(Et_4N)[Co(2\text{-}S\text{-}C_5H_4N)_3]$

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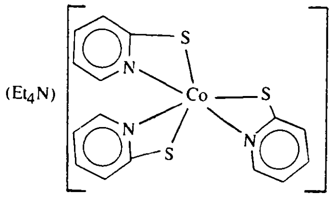
Abstract

$Na[Co(CO)_4]$ was reacted with pyridine-2-thiol (PyS) in tetrahydrofuran to give the title complex, $(C_8H_{20}N)$-$[Co(C_5H_4NS)_3]$, in which the three S atoms and the three N atoms of the PyS ligands coordinate to the central Co^{II} atom, forming three four-membered chelate rings with S—Co—N angles of 66°. The geometry around the Co^{II} atom is distorted octahedral. The average Co—S and Co—N bond distances are 2.568 and 2.108 Å, respectively.

Comment

Since low-valence cobalt was discovered to be a good hydrosulfurization catalyst, the study of the reactions of cobalt in low oxidation states, *e.g.* $[Co_2(CO)_8]$ and $[Co(CO)_4]^-$, with different types of organic and inorganic sulfur-containing compounds, has attracted increased attention from chemists (Doedens & Dahl, 1966). Most of the research work, however, has focused on monodentate or bidentate organic sulfur compounds, with only a few mixed bidentate organic sulfur compounds being studied. Pyridine-2-thiol (PyS) is known as either a monodentate ligand, which binds to the metal atom through the S atom (one-electron donor), or as a mixed bidentate ligand, which binds through both the S and the N atom (three-electron donor). While studying the reaction of $Na[Co(CO)_4]$ with PyS, we obtained a new type of cobalt–sulfur product with mixed-valence Co^I and Co^{III} atoms, $[Co_5(\mu_3\text{-}S)_3(\mu\text{-}CO)_2(PyS)_7]$, (*A*), and a Co^{II} compound, $(Et_4N)[Co(PyS)_3]$, (*B*). We report here the synthesis and crystal structure of compound (*B*).



(*B*)

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