Crystal structure of bis(diaqua-dicinnamatocopper(II)), $C_{36}H_{36}Cu_2O_{12}$

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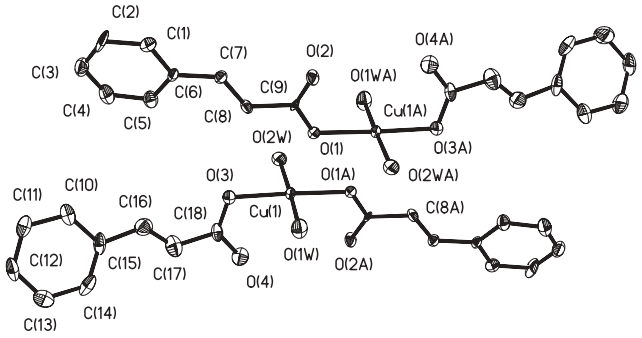

Abstract

$C_{36}H_{36}Cu_2O_{12}$, orthorhombic, *Pbca* (No. 61), $a = 10.992(1)$ Å, $b = 7.706(1)$ Å, $c = 41.770(5)$ Å, $V = 3538.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.109$, $wR_{ref}(F^2) = 0.269$, $T = 293$ K.

Source of material

All reagents and solvents were used as obtained without further purification. An aqua-ammonium solution (10 ml) of Cu_2O (71 mg, 0.5 mmol) and cinnamatic acid (147 mg, 1.0 mmol) were stood still for 1 week to vapor most of the ammonium gas, large blue slab crystals of the title complex were deposited and collected by filtration, washed with water and dried in a vacuum desiccator over silica gel (yield 67%). Elemental analysis: found – C, 54.66%; H, 4.66%; calc. for $C_{36}H_{36}Cu_2O_{12}$ – C, 54.89%; H, 4.61%.

Experimental details

All the hydrogen atoms are geometrically fixed excepting those attached to the water molecules which are located using the program HYDROGEN [1] and freely refined. We refined these hydrogen atoms to confirm that these are really water molecules and not OH or O atoms.

Discussion

Metal complexes with carboxylates are among the most investigated compounds in the field of coordination chemistry. Nevertheless, the crystal structures of metal complexes with cinnamate ligands have rarely been reported. Previously, we reported the structure and properties of a silver(I) comples $[Ag(\mu\text{-hmt})(cin)] \cdot 2H_2O$ (hmt = hexamethylenetetramine, cin = cinnamate) [2], with this organic carboxylic acid.

The title complex is a discrete electronically neutral dinuclear copper(II) unit, $[Cu(cinH)_2(H_2O)_2]_2$, where cinH is cinnamatic acid. The two copper(II) atoms in each dinuclear unit are equivalent, each of which is ligated by four oxygen atoms from two cinnamate anions and two coordinated water molecules, respectively. The four coordination atoms around the central metal are coplanar, constituting a square-planar geometry around the copper(II) atom with plane deviation of 0.0384(4) Å, and the copper atom is deviated from the square-plane by 0.0123(4) Å. All the cinnamate anions are unidentate ligands, and the average Cu-O(cinnamate) bond length (2.001(6) Å) is in the normal range for the complexes with aromatic carboxylates. The two diagonal angles in the CuO_4 square plane are respectively 175.8(3)° and 178.0(2)°, indicating a slightly distorted square-planar geometry of Cu(1). The Cu square plane is at the angles of 73.7(2)° and 123.4(2)° with the two kinds of aromatic rings. All the CuO_4 planes in the complex are parallel one another. Weak interactions play an important role in the crystal structure of the title complex. The shortest distance between the CuO_4 planes is 3.528(6) Å, and a great deal of hydrogen bonds between the adjacent O atoms join the two monomers to form a dinuclear copper(II) unit.

Table 1. Data collection and handling.

Crystal:	blue slab, size 0.06 × 0.24 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.65 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20956, 4397
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2212
$N(param)_{refined}$:	242
Programs:	SHELXTL [3], SHELXTL-plus [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*c*	–0.0137	0.9659	0.1160	0.057
H(2)	8*c*	–0.0383	0.8838	0.1683	0.078
H(3)	8*c*	0.1206	0.7573	0.1960	0.065
H(4)	8*c*	0.3001	0.7099	0.1705	0.060
H(5)	8*c*	0.3330	0.8065	0.1194	0.047
H(7)	8*c*	0.1043	0.9792	0.0674	0.034
H(8)	8*c*	0.3519	0.9345	0.0716	0.033
H(10)	8*c*	0.4710	0.8780	0.1946	0.068
H(11)	8*c*	0.4746	0.9165	0.2493	0.073
H(12)	8*c*	0.6345	1.0631	0.2727	0.072
H(13)	8*c*	0.7882	1.1667	0.2419	0.084
H(14)	8*c*	0.7803	1.1317	0.1865	0.070
H(16)	8*c*	0.5333	0.9393	0.1426	0.066
H(17)	8*c*	0.7683	1.0099	0.1368	0.078
H(1W1)	8*c*	0.50(2)	1.21(2)	0.048(4)	0.13(6)
H(1W2)	8*c*	0.509(8)	0.67(1)	0.027(2)	0.02(2)
H(2W1)	8*c*	0.628(9)	1.31(1)	0.016(2)	0.05(3)
H(2W2)	8*c*	0.619(8)	0.67(1)	0.056(2)	0.05(3)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	8*c*	0.59411(9)	0.9655(1)	0.03361(2)	0.0247(5)	0.0259(5)	0.0185(5)	–0.0017(5)	0.0018(4)	0.0034(4)
O(1)	8*c*	0.3834(5)	1.0086(7)	0.0137(1)	0.024(3)	0.029(3)	0.025(3)	–0.002(2)	0.000(2)	0.003(2)
O(2)	8*c*	0.1848(5)	1.0573(8)	0.0140(1)	0.027(3)	0.049(4)	0.029(4)	0.009(3)	–0.002(3)	0.012(3)
O(3)	8*c*	0.5765(5)	0.9451(9)	0.0812(1)	0.035(4)	0.052(4)	0.029(3)	–0.006(3)	0.000(3)	0.004(3)
O(4)	8*c*	0.7757(6)	0.9834(9)	0.0784(2)	0.040(4)	0.057(5)	0.053(4)	0.013(4)	0.005(4)	0.005(4)
O(1W)	8*c*	0.5970(9)	1.2251(9)	0.0387(2)	0.090(6)	0.032(4)	0.044(5)	–0.006(4)	–0.001(5)	0.001(3)
O(2W)	8*c*	0.5811(7)	0.709(1)	0.0308(2)	0.041(4)	0.056(5)	0.047(4)	–0.008(4)	–0.010(4)	0.013(4)
C(1)	8*c*	0.0513(9)	0.917(2)	0.1270(2)	0.032(5)	0.068(8)	0.042(6)	–0.011(5)	0.002(5)	0.009(5)
C(2)	8*c*	0.036(1)	0.867(2)	0.1582(3)	0.064(8)	0.09(1)	0.038(7)	–0.011(7)	0.035(6)	0.017(6)
C(3)	8*c*	0.131(1)	0.791(2)	0.1747(3)	0.077(9)	0.052(7)	0.033(6)	–0.022(6)	0.006(6)	0.006(5)
C(4)	8*c*	0.238(1)	0.766(1)	0.1596(2)	0.070(8)	0.044(7)	0.036(6)	0.004(6)	–0.009(6)	0.003(5)
C(5)	8*c*	0.257(1)	0.820(1)	0.1287(2)	0.050(6)	0.034(6)	0.034(5)	0.004(5)	–0.003(5)	0.004(4)
C(6)	8*c*	0.1636(8)	0.896(1)	0.1115(2)	0.028(5)	0.026(4)	0.020(4)	–0.003(4)	0.006(4)	0.002(3)
C(7)	8*c*	0.1755(7)	0.950(1)	0.0781(2)	0.023(4)	0.034(5)	0.027(4)	0.000(4)	0.001(4)	0.006(4)
C(8)	8*c*	0.2787(8)	0.960(1)	0.0615(2)	0.025(4)	0.037(5)	0.021(4)	0.005(4)	–0.006(3)	0.000(4)
C(9)	8*c*	0.2794(7)	1.0122(9)	0.0269(2)	0.026(4)	0.013(4)	0.017(4)	–0.007(3)	0.007(3)	0.006(3)
C(10)	8*c*	0.536(1)	0.938(2)	0.2038(2)	0.074(8)	0.064(8)	0.034(6)	0.009(6)	–0.006(6)	–0.002(5)
C(11)	8*c*	0.537(1)	0.960(2)	0.2368(3)	0.065(8)	0.072(8)	0.044(7)	0.005(7)	0.023(6)	0.004(6)
C(12)	8*c*	0.633(1)	1.047(2)	0.2506(3)	0.10(1)	0.051(7)	0.024(5)	0.007(7)	–0.002(6)	–0.004(5)
C(13)	8*c*	0.723(1)	1.109(2)	0.2325(3)	0.08(1)	0.064(8)	0.069(9)	–0.019(7)	–0.005(8)	–0.014(7)
C(14)	8*c*	0.718(1)	1.086(2)	0.1991(3)	0.065(8)	0.049(7)	0.059(8)	–0.001(6)	0.032(7)	0.014(6)
C(15)	8*c*	0.626(1)	1.000(1)	0.1845(2)	0.092(9)	0.026(6)	0.027(5)	0.011(5)	0.010(5)	0.006(4)
C(16)	8*c*	0.610(1)	0.971(2)	0.1497(3)	0.049(7)	0.058(7)	0.059(7)	–0.002(6)	–0.002(6)	0.009(6)
C(17)	8*c*	0.691(1)	0.985(2)	0.1291(3)	0.072(9)	0.076(9)	0.047(7)	0.014(7)	–0.001(6)	–0.005(6)
C(18)	8*c*	0.6797(9)	0.969(1)	0.0941(2)	0.049(6)	0.039(5)	0.024(5)	0.015(5)	–0.001(4)	0.006(4)

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