Refinement of the crystal structure of diaquabis(μ -succinato)dicopper(II) dihydrate, $\text{Cu}_2(\text{H}_2\text{O})_2(\text{C}_4\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$

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Received August 24, 2004, accepted and available on-line November 17, 2004; CCDC no. 1267/1386

Abstract

$\text{C}_4\text{H}_8\text{CuO}_6$, triclinic, $P\bar{1}$ (no. 2), $a = 6.4367(2)$ Å, $b = 7.6230(4)$ Å, $c = 8.0846(4)$ Å, $\alpha = 76.134(3)^\circ$, $\beta = 73.456(3)^\circ$, $\gamma = 81.476(3)^\circ$, $V = 367.8$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.035$, $wR_{\text{ref}}(F^2) = 0.091$, $T = 293$ K.

Source of material

Crystals of diaquabis(succinato)dicopper(II) dihydrate were unexpectedly formed during an experiment to synthesize the hetero-binuclear magnesium copper succinato complex. To a solution of succinic acid (4.724 g, 0.4 mol) in water (100 ml) MgCO_3 (1.686 g, 0.2 mol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (3.410 g, 0.2 mol) were added in small portions. The mixture was maintained with stirring for 30 minutes. The solution was kept at 40 °C and blue prismatic crystals grew by slow evaporation after three months. X-ray diffraction analysis indicated that no crystals of magnesium hetero-binuclear complex were formed, but crystals of the title compound.

Experimental details

Hydrogen atoms of water molecules were located from the Fourier difference maps and refined, those of methylene groups were only placed in calculated positions ($d_{\text{C-H}} = 0.95$ Å).

Discussion

Reported in this paper is a more accurate refinement of the known structure of the title compound presented by O'Connor and Maslen [1]. The molecular structure of copper(II) succinate shows it to be similar to copper(II) acetate [2]. The extended polymeric structure consists of chains of centrosymmetric dimeric units with a Cu...Cu separation of 2.6065(5) Å which is very close to that found in related binuclear copper(II) dicarboxylates. The Cu(II) atoms are pentacoordinated with the oxygen atom of water molecule assuming apical position and with four oxygen atoms of

four succinate anions assuming the basal positions in a tetragonal pyramidal arrangement. The distorted nature of the CuO_5 square pyramid can be understood from $\text{O}_{\text{succ}}\text{—Cu—O}_{\text{succ}}$ and $\text{O}_{\text{succ}}\text{—Cu—O}_{\text{water}}$ angles. While the former are found to be in the range $87.58(8)^\circ$ – $169.11(7)^\circ$, the latter are in the range $90.32(8)^\circ$ – $100.52(8)^\circ$. The Cu atom is 0.1867(9) Å from the mean plane formed by the four equatorial O atoms. On the other hand, the coordinated Ow1 atom lies in the same direction, at a distance of 2.302(2) Å from the plane. The bond lengths Cu—O_{succ} (ranging from 1.962(2) Å to 1.973(2) Å) are more shorter than the bond distance Cu—O_{water} of 2.124(2) Å. However, all these distances remain comparable to those of related binuclear copper dicarboxylates. Four bis-bidentate succinate anions form *syn-syn* bridges between two copper atoms of the same cage. This results of the formation of two eight-membered rings, which were almost planar (maximum deviation at O2 atom: 0.033(1) Å) and perpendicular to each other (dihedral angle: $88.54(4)^\circ$). The dimensions of the succinate ion is similar to the values found in previous structures containing this dicarboxylate ligand. The two carboxylate group planes are almost perpendicular to each other (dihedral angle $81.8(2)^\circ$) and to the plane of carbon skeleton (dihedral angles $89.2(1)^\circ$ and $88.2(2)^\circ$), respectively. The chain of binuclear units run parallel to the *a*-axis. The presence of water molecules of coordination (OW1) and crystallization (OW2) sets up a strong hydrogen bonding network between chains.

Table 1. Data collection and handling.

Crystal:	blue prism, size 0.10 × 0.14 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	29.50 cm ^{−1}
Diffractometer, scan mode:	Nonius KappaCCD, ω
$2\theta_{\text{max}}$:	60.1°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5628, 2129
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1858
$N(\text{param})_{\text{refined}}$:	113
Programs:	SHELXL-97 [3], ORTEP-3 [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2A)	2i	1.0274	0.8563	−0.3366	0.029
H(2B)	2i	0.9516	0.7899	−0.4730	0.029
H(3A)	2i	0.6932	0.3204	0.4987	0.032
H(3B)	2i	0.8301	0.4837	0.4217	0.032
HW(1A)	2i	0.139(5)	0.889(5)	0.165(4)	0.033
HW(1B)	2i	0.268(5)	0.985(5)	0.127(4)	0.033
HW(2A)	2i	0.272(5)	0.198(4)	−0.229(4)	0.033
HW(2B)	2i	0.259(5)	0.016(5)	−0.218(4)	0.033

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu	2i	0.42117(4)	0.65496(3)	0.04379(3)	0.0203(2)	0.0175(2)	0.0238(2)	−0.0017(1)	−0.0057(1)	−0.0059(1)
O(1)	2i	0.6737(3)	0.7654(2)	−0.1326(2)	0.0258(8)	0.0221(8)	0.034(1)	−0.0051(6)	0.0012(7)	−0.0064(7)
O(2)	2i	0.5947(3)	0.5821(2)	0.2185(2)	0.0301(8)	0.0293(9)	0.0306(9)	0.0007(7)	−0.0137(7)	−0.0081(7)
O(3)	2i	0.1934(3)	0.5033(2)	0.2020(2)	0.0258(8)	0.0230(9)	0.035(1)	−0.0074(6)	−0.0007(7)	−0.0058(7)
O(4)	2i	0.2808(3)	0.6884(3)	−0.1496(2)	0.0374(9)	0.032(1)	0.031(1)	0.0028(7)	−0.0181(8)	−0.0109(8)
OW(1)	2i	0.2470(3)	0.8870(3)	0.1361(3)	0.030(1)	0.028(1)	0.076(2)	−0.0017(9)	0.002(1)	−0.026(1)
OW(2)	2i	0.2036(4)	0.1122(3)	−0.2546(3)	0.054(1)	0.035(1)	0.074(2)	−0.004(1)	−0.034(1)	−0.007(1)
C(1)	2i	0.8125(3)	0.6641(3)	−0.2214(3)	0.021(1)	0.023(1)	0.022(1)	−0.0046(8)	−0.0089(8)	−0.0021(8)
C(2)	2i	0.9965(3)	0.7518(3)	−0.3668(3)	0.025(1)	0.024(1)	0.022(1)	−0.0051(8)	−0.0075(9)	−0.0001(9)
C(3)	2i	0.7971(4)	0.3764(3)	0.3978(3)	0.022(1)	0.036(1)	0.020(1)	−0.0035(9)	−0.0048(9)	−0.006(1)
C(4)	2i	0.6985(3)	0.4269(3)	0.2431(3)	0.0173(9)	0.027(1)	0.021(1)	−0.0044(8)	−0.0025(8)	−0.0052(9)

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