Crystal structure of aqua-ammine-(μ -succinato)copper(II) dihydrate, $\text{Cu}(\text{H}_2\text{O})(\text{NH}_3)(\text{C}_4\text{H}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$

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Abstract

$\text{C}_4\text{H}_{13}\text{CuNO}_7$, monoclinic, $P12/c1$ (no. 13), $a = 8.434(3)$ Å, $b = 7.230(3)$ Å, $c = 8.309(3)$ Å, $\beta = 112.209(5)^\circ$, $V = 469.1$ Å³, $Z = 2$, $R_g(F) = 0.020$, $wR_{\text{ref}}(F^2) = 0.051$, $T = 293$ K.

Source of material

Crystals of aqua-ammine-(μ -succinato)copper(II) dihydrate were unexpectedly formed during an attempt to synthesize the mixed ligand copper complex. A mixture of copper chloride dihydrate (34.2 mg, 0.2 mmol), NaOH (16 mg, 0.4 mmol), succinic acid (23.6 mg, 0.2 mmol), and 5,7-dimethyl-1,8-naphthyridine-2-amine (35 mg, 0.2 mmol), in ethanol (10 ml) was refluxed for 1 h. The resulted light blue precipitate was collected and dissolved in 3 ml of concentrated ammonia. Blue block-like crystals were obtained by slow evaporation of the ammonia solution at ambient temperature.

Experimental details

Hydrogen atoms of methylene groups were only placed in corresponding calculated positions [$d(\text{C}—\text{H}) = 0.97$ Å]. Positions of hydrogen atoms of water and ammonia molecules were located from the difference Fourier syntheses and refined. All U_{iso} values were restrained on U_{eq} values of the parent atoms.

Discussion

Carboxylate complexes have been much investigated in recent years due to their interesting coordination chemistry allowing for unusual structural features and leading to various physical and chemical properties and practical applications [1–4]. Among them copper(II) carboxylates are of special interest as they are easily obtained as polynuclear units having relevance to magnetic materials [5] and biology [6]. Our research is focussed on carboxylate coordination compounds [7,8].

In the title crystal structure, each Cu atom is coordinated by two oxygen atoms of two different succinato ligands, one water oxygen atom, and one ammonia nitrogen atoms to complete CuO_3N square plane. The succinate dianions are maximally extended (C—

C—C torsion angle is 177.44°) and link Cu atoms in bis-monodentate fashion to generate infinite chains along [101]. As expected, the C—O distance to the coordinating O atoms is $1.281(4)$ Å, which is significantly longer than that to the non-coordinating one ($1.230(4)$ Å). Cu1—N1 bond distance ($2.06(2)$ Å) is comparable with some known Cu dicarboxylates [9]. The Cu—O bond distances range from $1.95(1)$ to $1.966(2)$ Å which agree well with the already reported result. In addition the $d(\text{Cu}—\text{O}_{\text{succ}})$ is longer than the $d(\text{Cu}—\text{O}_{\text{water}})$. The O—Cu—O ($\text{O}3—\text{Cu}1—\text{O}1$, $89.1(5)^\circ$) bond angles are close to 90° , and O—Cu—N ($\text{O}3—\text{Cu}1—\text{N}1$, $180.000(5)^\circ$) bond angles close to 180° imply the CuO_3N moiety to be highly square planar. The Cu—Cu separation within the chain is of 9.338 Å, which is shorter than the reported values [9]. The presence of water (coordination and crystallization) and ammonia molecules sets up a strong hydrogen bonding network between the chains.

Table 1. Data collection and handling.

Crystal:	blue block, size $0.21 \times 0.35 \times 0.39$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	23.37 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	50.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1187, 444
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 443
$N(\text{param})_{\text{refined}}$:	56
Programs:	SHELXS-97 [10], SHELXL-97 [11], SHELXTL [12]

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

Atom	Site	Occ.	x	y	z	U_{iso}
O(3)	2f		$\frac{1}{2}$	$-0.021(1)$	$\frac{3}{4}$	$0.027(2)$
H(1)	4g	0.50	0.4308	-0.0647	0.7926	0.041
H(2)	4g	0.50	0.5951	-0.0633	0.8201	0.041
N(1)	2f		$\frac{1}{2}$	$0.529(3)$	$\frac{3}{4}$	$0.085(6)$
H(1A)	4g	0.50	0.5712	0.5700	0.8530	0.127

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(1B)	4g	0.50	0.3947	0.5700	0.7297	0.127
H(1C)	4g	0.50	0.5341	0.5700	0.6673	0.127
H(3)	4g		0.8091	0.2782	0.6599	0.080

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(4)	4g		0.8842	0.2156	0.5535	0.080
H(2A)	4g		0.1224	0.3459	0.2208	0.061
H(2B)	4g		0.1225	0.1296	0.2214	0.061

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(1)	2f	½	0.248(3)	¾	0.0218(3)	0.0279(5)	0.0201(3)	0	0.0039(2)	0
O(1)	4g	0.3614(3)	0.253(2)	0.4995(3)	0.026(1)	0.054(2)	0.024(1)	−0.018(5)	0.0052(8)	−0.014(5)
O(2)	4g	0.1388(3)	0.224(3)	0.5767(3)	0.033(1)	0.06(1)	0.022(1)	0.003(2)	0.0095(8)	−0.001(2)
O(4)	4g	0.7879(4)	0.222(3)	0.5641(4)	0.040(1)	0.09(1)	0.031(1)	−0.015(3)	0.009(1)	−0.010(3)
C(1)	4g	0.2009(4)	0.238(2)	0.4650(4)	0.029(2)	0.049(3)	0.018(1)	0.012(4)	0.003(1)	0.000(4)
C(2)	4g	0.0927(4)	0.238(2)	0.2729(4)	0.033(2)	0.094(5)	0.019(1)	0.031(5)	0.002(1)	−0.014(4)

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