Crystal structure of poly-[(3-hydroyxpyridine)oxalatocopper(II)] monohydrate, $Cu(NC_5H_4OH)(COO)_2 \cdot H_2O$

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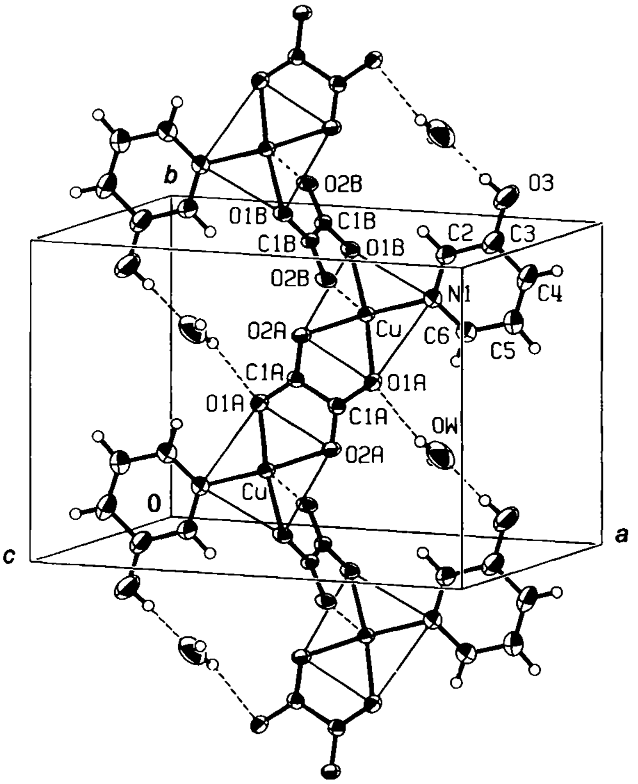

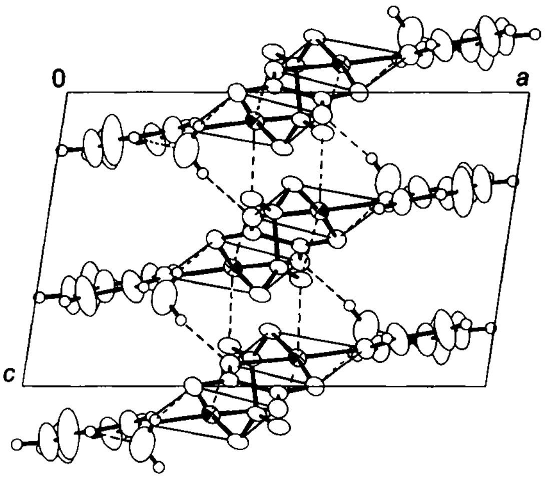

Abstract

$C_7H_7CuNO_6$, monoclinic, $P12_1/c1$ (no. 14), a = 12.9147(8) Å, b = 9.1615(6) Å, c = 8.2474(5) Å, β = 98.490(5)°, V = 965.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.079, T = 293 K.

Source of material

The new phase emerged as a by-product from a synthesis as described in [1]. 3 mmol (0.285 g) of 3-hydroxypyridine (pyOH = C_5H_5NO) were dissolved in 20 ml distilled water and 1 mmol (0.354 g) of $K_2Cu(ox)_2 \cdot 2H_2O$ (ox = oxalate) was dissolved in 60 ml water, both under continuous stirring at slightly elevated temperature. 3-hydroxypyridine was a commercial product, but $K_2Cu(ox)_2 \cdot 2H_2O$ was prepared as a well crystallized precipitate from aqueous solutions of $K_2(ox) \cdot H_2O$ and $CuCl_2 \cdot 2H_2O$ in the molar ratio 2:1. The pyOH solution was then added dropwise to the stirred potassium copper oxalate solution. The light blue solution was allowed to stand at room temperature. After three weeks two different crystal phases began to grow by evaporation of the solvent: (i) first, light-green elongated platelets formed with composition $(pyOH)Cu(ox) \cdot H_2O$. They proved to be a new phase, which is presented here. (ii) Afterwards blue crystals formed with isometric shape. They could be identified by means of X-ray diffraction as orthorhombic $(pyOH)_2Cu(ox)$ [1].

Experimental details

The hydrogen atom HW1 of the water molecule, which is not involved in hydrogen bonding, could hardly be located by difference Fourier analysis. The H—O bond distances and the H–O–H bond angle were restrained to idealized values in order to achieve reasonable bond data. The rigid water molecule was allowed to translate and rotate freely during the refinement procedure. The isotropic displacement parameters of HW1 and HW2 were fixed at 1.5 times the U_{eq} of OW.

Discussion

The crystal structure of the title compound is built up by copper oxalate chains extending along the b axis (figure, top). There are two inequivalent oxalate molecules, ox-A and ox-B. Both are centrosymmetric and have their planes nearly perpendicular to each other. Ox-A has all four oxygen atoms coordinated to two adjacent Cu ions. The carboxylate groups are delocalized with nearly equal bond distances d(O1A—C1A) = 1.253(2) Å and d(O2A—C1A) = 1.252(2) Å. The second oxalate molecule ox-B shows different bond lengths of the carboxylate group, namely d(O1B—C1B) = 1.268 Å and d(O2B—C1B) = 1.237 Å, where the single-bonded O1B is coordinated to Cu, but the double-bonded O2B has only close contacts to two Cu ions, one in the same chain (2.349 Å) and the second in the neighboring chain (2.405 Å). These close contacts connect the chains to layers parallel to (100), as indicated in the bottom part of the figure. The layers are separated by the pyridine rings. The Cu coordination is square planar and consists of three oxalate oxygen atoms O1A, O2A, O1B and the pyridine N at distances in the range 1.980 Å – 2.005 Å. The two next nearest oxygen atoms (O2B) in the apical positions complete this coordination to a distorted octahedron. The water mole-

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cule is situated in the large cavity between the pyridine rings, fixed by hydrogen bonds to oxalate (d(OW–HW2···O2A) = 2.891 Å) and the hydroxy group of the pyOH ring (d(O3–H3···OW) = 2.657 Å).

The main differences between the new crystal species described in this work and the blue orthorhombic phase [1] and its isomorphous cobalt and nickel compounds [2] are: (i) The blue phase has two hydroxypyridine molecules instead of one in the new phase, attached to each copper atom, which leads to a completely different stacking of the chains. (ii) The intrachain copper-copper distances are similar in both compounds, 5.548 Å in the blue phase and 5.223 Å (across ox-A) and 5.610 Å (across ox-B) in the title compound. The shortest interchain copper-copper distance is as large as 8.743 Å in the blue phase, whereas in our new phase it is only 4.130 Å, leading to the two-dimensional connectivity.

Table 1. Data collection and handling.

Crystal:	light green plate, size 0.03 × 0.16 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	22.71 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Xcalibur3 & Sapphire2 CCD, φ/ω
$2\theta_{max}$:	55.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14740, 2321
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1948
$N(param)_{refined}$:	162
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-3 [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4e	0.287(2)	0.504(3)	0.105(3)	0.041(7)
H(3)	4e	0.160(4)	0.671(7)	0.157(7)	0.14(2)
H(4)	4e	0.007(3)	0.394(4)	0.199(4)	0.07(1)
H(5)	4e	0.062(3)	0.146(4)	0.212(4)	0.08(1)
H(6)	4e	0.227(2)	0.099(3)	0.163(4)	0.049(8)
H(W1)	4e	0.702(3)	0.350(5)	0.386(5)	0.106
H(W2)	4e	0.682(4)	0.267(4)	0.224(5)	0.106

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	4e	0.41553(2)	0.23749(3)	0.09684(3)	0.0281(2)	0.0183(2)	0.0252(1)	–0.0000(1)	0.00806(9)	–0.0019(1)
O(1A)	4e	0.3686(1)	0.0432(2)	0.0007(2)	0.0287(7)	0.0246(8)	0.0286(7)	0.0008(6)	0.0074(6)	–0.0042(6)
O(2A)	4e	0.5586(1)	0.1621(2)	0.0751(2)	0.0329(7)	0.0189(8)	0.0291(7)	–0.0022(6)	0.0071(6)	–0.0031(6)
C(1A)	4e	0.5547(2)	0.0340(2)	0.0220(2)	0.029(1)	0.022(1)	0.0184(8)	–0.0007(8)	0.0059(7)	0.0013(7)
O(1B)	4e	0.4829(1)	0.4199(2)	0.1880(2)	0.0396(8)	0.0204(7)	0.0192(6)	–0.0036(6)	0.0092(6)	0.0005(6)
O(2B)	4e	0.5664(1)	0.6244(2)	0.1373(2)	0.0421(8)	0.0213(8)	0.0215(7)	–0.0074(6)	0.0068(6)	–0.0003(6)
C(1B)	4e	0.5147(2)	0.5138(2)	0.0937(2)	0.029(1)	0.018(1)	0.0176(9)	0.0025(8)	0.0059(7)	–0.0020(7)
O(3)	4e	0.1129(2)	0.6158(3)	0.1620(5)	0.043(1)	0.040(1)	0.210(4)	0.011(1)	0.039(2)	–0.010(2)
N(1)	4e	0.2711(1)	0.2943(2)	0.1282(2)	0.0302(9)	0.027(1)	0.0336(9)	0.0014(8)	0.0094(7)	0.0006(8)
C(2)	4e	0.2407(2)	0.4327(3)	0.1276(3)	0.033(1)	0.027(1)	0.057(2)	0.002(1)	0.012(1)	0.001(1)
C(3)	4e	0.1429(2)	0.4746(3)	0.1594(4)	0.036(1)	0.039(2)	0.088(2)	0.006(1)	0.016(1)	–0.008(2)
C(4)	4e	0.0734(2)	0.3679(4)	0.1898(5)	0.037(2)	0.052(2)	0.117(3)	0.003(1)	0.031(2)	–0.013(2)
C(5)	4e	0.1059(3)	0.2254(4)	0.1929(6)	0.047(2)	0.046(2)	0.133(4)	–0.007(1)	0.046(2)	–0.001(2)
C(6)	4e	0.2042(2)	0.1914(3)	0.1610(4)	0.047(2)	0.030(1)	0.085(2)	0.001(1)	0.032(1)	0.002(2)
O(W)	4e	0.7237(2)	0.2952(3)	0.3022(4)	0.049(1)	0.060(2)	0.100(2)	0.005(1)	0.004(1)	–0.027(1)

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