Crystal structure of polymeric aqua-pyridine-μ_4-squarato-copper(II), $[Cu(C_5H_5N)(C_4O_4)(H_2O)]$

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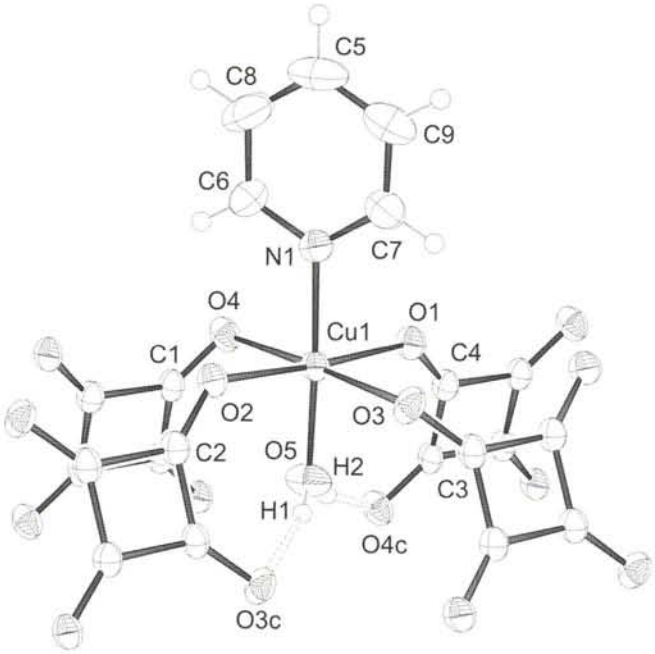

Abstract

$C_9H_7CuNO_5$, monoclinic, $P12_1/n1$ (No. 14), $a = 5.940(1)$ Å, $b = 8.214(1)$ Å, $c = 19.440(3)$ Å, $\beta = 92.18(1)°$, $V = 947.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.039$, $wR_{ref}(F^2) = 0.108$, $T = 293$ K.

Source of material

Single crystals suitable for X-ray analysis have been obtained by mixing 10 ml of 0.04 M copper(II) acetate solution with 10ml sodium metasilicate solution (1.06 g/ml, pH 5.0). After three days the gelling process is finished and a solution, containing 0.02 M sodium-squarate and 0.02 m pyridine, was placed over the set gel. Within one week well developed dark green crystals are formed on the gel-solution interface.

Experimental details

During structure refinement, hydrogenatoms bond to the coordinated water molecule were located directly from the difference Fourier synthesis. The remaining H-atoms (pyridine) were geometrically set as idealized aromatic C-H groups using a riding model.

Discussion

Recently we reported about the crystal growth and structure determination of polymeric diaqua-bis(pyridine)-μ_2-squarato(1,3)-copper(II) [1]. We have now been able to obtain a different coordination copper(II) compound containing pyridine and the bridging squarate-dianion, from the same set of experiments. The crystal structure of the title compound $[Cu(C_5H_5N)(C_4O_4)(H_2O)]$ is based on copper(II) double layers perpendicular to the *c*-direction, with squarate-anions acting as μ_4-bridging ligands. The monodentate pyridine molecules are located between the resulting coppersquarate layers. Every copper-ion is therefore coordinated in distorted octahedral manner by four squarate anions, one pyridine as well as one water molecule, which is "trapped" inside the coppersquarate layer. The water molecule (O5) is stabilized by forming two hydrogen bonds with two nearby squarate-oxygen atoms (O5—H1—O3 and O5—H2—O4).

Table 1. Data collection and handling.

Crystal:	dark green, blocks, size 0.3 × 0.6 × 0.7 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	23.08 cm^{-1}
Diffractometer, scan mode:	Philips PW 1100 STOE-modified, $\omega/2\theta$
$2\theta_{max}$:	55.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4492, 2184
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1776
$N(param)_{refined}$:	153
Programs:	SHELXS-97 [2], SHELXL-97 [3], PLATON92 [4]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5)	4*e*	0.5449	0.2371	0.3706	0.070
H(6)	4*e*	0.2244	0.3564	0.1933	0.054
H(7)	4*e*	0.8129	0.1473	0.1895	0.052
H(8)	4*e*	0.2392	0.3508	0.3120	0.074
H(9)	4*e*	0.8356	0.1297	0.3078	0.070
H(1)	4*e*	0.443(8)	0.185(6)	–0.040(2)	0.06(2)
H(2)	4*e*	0.534(9)	0.317(6)	–0.042(3)	0.06(2)

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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)	4*e*	0.50305(6)	0.25401(5)	0.07824(2)	0.0212(2)	0.0266(2)	0.0250(3)	–0.0078(2)	0.0016(2)	–0.0006(2)
O(1)	4*e*	0.7924(4)	0.3746(3)	0.0819(1)	0.022(1)	0.035(1)	0.032(1)	–0.0117(9)	0.0033(9)	0.001(1)
O(2)	4*e*	0.2115(4)	0.1361(3)	0.0825(1)	0.022(1)	0.035(1)	0.032(1)	–0.0124(9)	0.0027(9)	–0.004(1)
O(3)	4*e*	0.7043(4)	0.0030(3)	0.0724(1)	0.024(1)	0.033(1)	0.039(1)	–0.0088(9)	0.011(1)	–0.007(1)
O(4)	4*e*	0.2934(4)	0.5143(3)	0.0795(1)	0.025(1)	0.034(1)	0.034(1)	–0.0097(9)	–0.003(1)	0.006(1)
N(1)	4*e*	0.5177(5)	0.2505(3)	0.1801(2)	0.030(1)	0.027(1)	0.029(2)	–0.008(1)	0.003(1)	–0.001(1)
O(5)	4*e*	0.4753(5)	0.2616(4)	–0.0211(2)	0.054(2)	0.037(2)	0.030(2)	–0.027(1)	0.003(1)	–0.001(1)
C(1)	4*e*	0.1340(5)	0.5067(4)	0.0359(2)	0.018(1)	0.022(1)	0.033(2)	–0.004(1)	0.003(1)	–0.001(1)
C(2)	4*e*	0.0977(5)	0.0627(4)	0.0363(2)	0.021(1)	0.020(1)	0.030(2)	–0.003(1)	0.001(1)	0.001(1)
C(3)	4*e*	0.8668(5)	0.0013(4)	0.0326(2)	0.019(1)	0.022(1)	0.033(2)	–0.004(1)	0.000(1)	–0.000(1)
C(4)	4*e*	0.9034(5)	0.4422(4)	0.0357(2)	0.021(1)	0.021(1)	0.032(2)	–0.003(1)	0.003(1)	–0.002(1)
C(5)	4*e*	0.538(1)	0.2403(6)	0.3227(2)	0.090(4)	0.059(3)	0.026(2)	–0.029(3)	–0.002(2)	0.003(2)
C(6)	4*e*	0.3491(7)	0.3110(5)	0.2165(2)	0.041(2)	0.057(2)	0.037(2)	–0.003(2)	0.011(2)	–0.000(2)
C(7)	4*e*	0.6943(7)	0.1872(5)	0.2145(2)	0.042(2)	0.048(2)	0.040(2)	0.001(2)	–0.005(2)	–0.001(2)
C(8)	4*e*	0.3573(9)	0.3074(7)	0.2879(3)	0.071(3)	0.076(3)	0.040(3)	–0.010(3)	0.023(2)	–0.009(2)
C(9)	4*e*	0.7108(9)	0.1775(6)	0.2857(2)	0.069(3)	0.061(3)	0.043(3)	–0.002(2)	–0.018(2)	0.008(2)

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