Refinement of the crystal structure of bis(*N,N*-dimethylformamide)-tetra(μ -formato)dicopper(II), $\text{Cu}_2(\text{HCOO})_4[(\text{CH}_3)_2\text{NCHO}]_2$, at 193 K

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Abstract

$\text{C}_{10}\text{H}_{18}\text{Cu}_2\text{N}_2\text{O}_{10}$, triclinic, $P\bar{1}$ (no. 2), $a = 6.440(1)$ Å, $b = 7.272(2)$ Å, $c = 9.819(2)$ Å, $\alpha = 100.327(4)^\circ$, $\beta = 98.781(3)^\circ$, $\gamma = 110.274(3)^\circ$, $V = 412.7$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.024$, $wR_{\text{ref}}(F^2) = 0.068$, $T = 193$ K.

Source of material

0.20 g $\text{Cu}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ was added to 10 ml dimethylformamide (DMF) with continuous stirring for 30 min, and then the solution was filtered. Blue single crystals were obtained ten days later.

Discussion

The crystal structure of the title compound was determined by Cejudo et al. at room temperature [1]. We have refined it at 193(2) K under the atmosphere of liquid nitrogen in order to get accurate crystal parameters at low temperature. The title structure consists of binuclear $[\text{Cu}_2(\text{DMF})_2(\text{HCOO})_4]$ units. The coordination environment at each copper atom is distorted square-pyramidal. The basal plane consists of four oxygen atoms from four formate anions, while the axial coordination site is occupied by an oxygen atom from a DMF molecule. The

$\text{Cu}-\text{O}(\text{formato})$ bond lengths, $\text{Cu1}-\text{O1}$, $\text{Cu1}-\text{O2A}$, $\text{Cu1}-\text{O3}$ and $\text{Cu1}-\text{O4A}$, are equal 1.969(2) Å, 1.976(2) Å, 1.964(2) Å and 1.972(2) Å, respectively, in the range from 1.964(2) Å to 1.976(2) Å, similar to the $\text{Cu}-\text{O}(\text{formate})$ bond lengths in $[\text{Cu}_2(\text{H}_2\text{O})(\text{HCOO})_4(\text{C}_{10}\text{H}_9\text{N}_3)] \cdot \text{H}_2\text{O}$ in which the $\text{Cu}(\text{II})$ atom has also a distorted square-pyramidal $\text{CuN}_2\text{O}_2\text{O}$ environment [2], and are different from the corresponding values in $[\text{Cu}(\text{HCOO})_2\text{L}]$ ($\text{L} = \text{pyrazine}$, 4,4'-bipyridine) which consists of tetragonally elongated CuN_2O_4 chromophore [3]. The $\text{Cu1}-\text{O5}$ bond length in the apical position is 2.135(2) Å, obviously longer than the corresponding values in basal plane. The O1 , O2A , O3 and O4 atoms deviate from the mean basal plane by -0.0020 Å ($2\times$) and 0.0020 Å ($2\times$), respectively. However, the Cu1 and O5 atoms deviate from the mean basal plane by 0.2013 Å and 0.3355 Å, respectively. The formate anions act as bis-monodentate bridging between two copper atoms and form the dimer structure. The $\text{Cu}-\text{Cu}$ bond length is 2.6505(6) Å. At RT the $\text{Cu}-\text{O}(\text{formato})$ bond distances are 1.959(3) Å, 1.967(3) Å, 1.969(3) Å and 1.973(3) Å, the $\text{Cu}-\text{O}(\text{DMF})$ bond length is 2.131(3) Å, and the $\text{Cu}-\text{Cu}$ bond length is 2.651(2) Å [1]. The R values and the remaining electron difference density peak heights (0.366 e Å⁻³, -0.459 e Å⁻³) in our work are significantly smaller than those values of the previous study ($R_{\text{gt}}(F) = 0.046$, $wR_{\text{ref}}(F^2) = 0.119$; 0.910 e Å⁻³ and -0.977 e Å⁻³, respectively [1]).

Table 1. Data collection and handling.

Crystal:	blue block, size $0.26 \times 0.29 \times 0.58$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	26.29 cm ⁻¹
Diffraction, scan mode:	Rigaku AFC-8 & Mercury CCD, ω
$2\theta_{\text{max}}$:	50.68°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4015, 1499
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1430
$N(\text{param})_{\text{refined}}$:	110
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2i	-0.4224	0.1706	0.1198	0.030
H(2)	2i	-0.2173	0.8722	0.0648	0.032
H(3A)	2i	0.5975	0.6379	0.2852	0.027
H(4A)	2i	0.4473	0.8078	0.5863	0.048
H(4B)	2i	0.7048	0.9528	0.6645	0.048
H(4C)	2i	0.6030	0.7260	0.6815	0.048
H(5A)	2i	0.9338	0.6877	0.4228	0.055
H(5B)	2i	0.9153	0.6485	0.5766	0.055
H(5C)	2i	1.0186	0.8752	0.5595	0.055

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Table 3. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu(1)	2i	0.12746(4)	0.57136(4)	0.13174(3)	0.0142(2)	0.0243(2)	0.0157(2)	0.0074(1)	−0.0007(1)	0.0037(1)
O(1)	2i	−0.1321(3)	0.3790(3)	0.1821(2)	0.0236(9)	0.034(1)	0.0245(9)	0.0038(8)	0.0043(7)	0.0104(7)
O(2)	2i	−0.3431(3)	0.2509(3)	−0.0424(2)	0.0182(8)	0.037(1)	0.0243(9)	0.0015(7)	0.0040(7)	0.0049(7)
O(3)	2i	−0.0194(3)	0.7674(3)	0.1525(2)	0.0246(9)	0.0306(9)	0.0279(9)	0.0149(7)	−0.0004(7)	−0.0005(7)
O(4)	2i	−0.2313(3)	0.6494(3)	−0.0727(2)	0.035(1)	0.040(1)	0.0253(9)	0.0264(9)	−0.0014(8)	0.0038(8)
O(5)	2i	0.3462(3)	0.6807(3)	0.3399(2)	0.0189(8)	0.0315(9)	0.0208(8)	0.0100(7)	−0.0013(7)	0.0039(7)
N(1)	2i	0.6776(3)	0.7431(3)	0.4920(2)	0.019(1)	0.026(1)	0.021(1)	0.0068(8)	−0.0019(8)	0.0069(8)
C(1)	2i	−0.3055(4)	0.2618(4)	0.0881(3)	0.021(1)	0.026(1)	0.029(1)	0.008(1)	0.010(1)	0.007(1)
C(2)	2i	−0.1591(4)	0.7687(4)	0.0492(3)	0.022(1)	0.028(1)	0.035(1)	0.015(1)	0.006(1)	0.007(1)
C(3)	2i	0.5421(4)	0.6826(3)	0.3638(2)	0.023(1)	0.024(1)	0.018(1)	0.0072(9)	0.0009(9)	0.0061(9)
C(4)	2i	0.6020(5)	0.8131(4)	0.6162(3)	0.039(2)	0.033(1)	0.018(1)	0.015(1)	−0.005(1)	−0.002(1)
C(5)	2i	0.9050(4)	0.7382(4)	0.5146(3)	0.021(1)	0.048(2)	0.040(2)	0.012(1)	−0.002(1)	0.019(1)

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