Refinement of crystal structure of copper acetate diammine, $Cu(CH_3COO)_2 \cdot 2NH_3$

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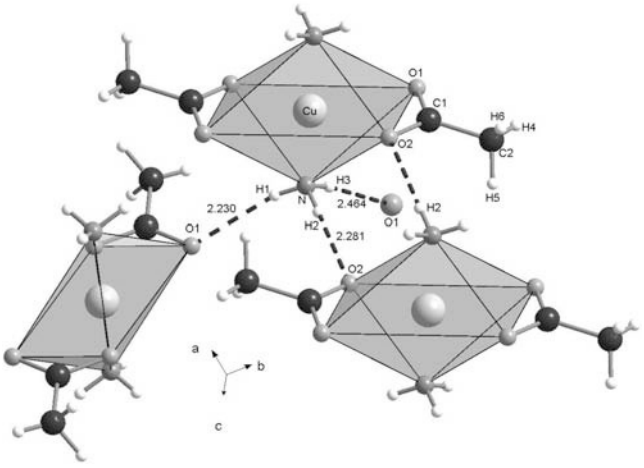

Abstract

$C_4H_{12}CuN_2O_4$, monoclinic, $P12_1/c1$ (no. 14), $a = 5.452(2)$ Å, $b = 10.220(5)$ Å, $c = 7.518(5)$ Å, $\beta = 107.067(3)°$, $V = 400.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.032$, $wR_{ref}(F^2) = 0.082$, $T = 295$ K.

Source of material

A first structure determination of the title compound was reported, based on intensities estimated from Weissenberg film exposures [1]. Our interest in historical pigment production prompted a reinvestigation because copper acetate diammine may occur as a byproduct in the synthesis of verdigris. Crystals of the title compound where obtained following the procedure to synthesize a basic copper acetate as a verdigris compound [2]: a nearly saturated solution of copper acetate monohydrate (Fluka) was heated up to 85 °C. Upon dropwise adding a 6 M solution of ammonium hydroxide, a fine precipitate appeared, which crystallized after cooling to deep blue copper acetate diammine.

Experimental details

The crystal decomposed during data collection. The sum of the intensities of the two standard reflections, remeasured after every 50, decreased by about 64.0 %. Therefore, the measurement stopped before full completion, explaining the low $N_{gt}/N_{parameter}$ ratio. Upon adjusting to the standard intensity decrease, the initial internal agreement factor $R(F^2)_{int}$ decreased from 19.9 % to 5.7 %.

Discussion

The copper atom occupying the inversion centre is coordinated by a heavily distorted octahedron, whose basal plane is defined by the O2 [d(Cu—O2) = 2.005(2) Å] and the N atoms [d(Cu—N) = 1.977(1) Å] of two acetate and two NH_3 groups, respectively, while the apices are given by the other acetate oxygen atoms O1 [d(Cu—O1) = 2.680(3) Å]. Thus, O1 and O2 of each acetate define one polyhedron edge and the different Cu—O bond strengths conform with the different distances C1—O1 of 1.240(3) Å and C1—O2 of 1.276(3) Å. Apart from O and N defining the basal plane, such Cu coordination is due to dsp^2-bonding as well known from other structures, e.g., $CuCl_2$, $CuBr_2$ [3,4]. The vertical and lateral degree of distortion of the coordination octahedron can also be seen from the bond angles subtended at Cu which vary between ∠O1–Cu–O2 = 53.77(1)°, ∠O1–Cu–N = 89.49(1)°, and ∠O2–Cu–N = 88.23(1)°. Compared to crystal structure of copper acetate monohydrate [5,6] and the chromium acetate dihydrate structures [7], there is no Cu-Cu interaction because the shortest Cu-Cu distance is 5.452(2) Å. The crystal structure is characterized by layers of isolated octahedra parallel to (100), which are held together by three weak hydrogen bonds, one for each H atom of NH_3 with d(O1···H1) = 2.23(4) Å, d(H1–N) = 0.77(4) Å, d(O1···N) = 2.984(4) Å, ∠N–H1–O1 166(3)°, d(O2···H2) = 2.28(5) Å, d(H2–N) = 0.81(4) Å, d(O2···N) = 3.087(4) Å, ∠N–H2–O2 = 175(4)°, d(O1···H3) = 2.46(4) Å, d(H3–N) = 0.86(4) Å, d(O1···N) = 3.318(4) Å, ∠N–H3–O1 = 172(3)°. Since O1 is connected with H1 and H3 of two different NH_3 groups in different layers, the hydrogen bond system provides three-dimensional framework. The large displacement parameters of the methyl hydrogen atoms H4, H5, H6 indicate significant disorder, which may be due to a torsional oscillation as suggested for copper acetate monohydrate [6].

Table 1. Data collection and handling.

Crystal:	blue plate, size 0.18 × 0.4 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	26.98 cm^{-1}
Diffractometer, scan mode:	RIGAKU AFC-6R, ω
$2\theta_{max}$:	50.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1378, 714
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 593
$N(param)_{refined}$:	77
Programs:	SHELXS-97 [8], SHELXL-97 [9], DIAMOND [10]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.526(6)	0.073(4)	0.202(4)	0.03(1)
H(4)	4*e*	0.983(7)	–0.383(4)	0.603(5)	0.06(1)
H(3)	4*e*	0.581(7)	–0.054(4)	0.203(5)	0.04(1)
H(2)	4*e*	0.746(9)	0.034(4)	0.293(5)	0.05(1)
H(5)	4*e*	0.161(8)	–0.268(4)	0.577(5)	0.08(1)
H(6)	4*e*	0.10(1)	–0.291(6)	0.752(8)	0.12(2)

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	2*d*	½	0	½	0.0171(3)	0.0242(4)	0.0320(4)	0.0024(2)	0.0064(2)	0.0012(2)
O(1)	4*e*	0.5756(4)	–0.2589(2)	0.4947(3)	0.023(1)	0.038(1)	0.060(1)	–0.003(1)	0.0054(8)	–0.0121(9)
O(2)	4*e*	0.8328(3)	–0.0939(2)	0.6105(2)	0.0212(9)	0.026(1)	0.042(1)	0.0026(8)	0.0072(8)	0.0026(8)
N	4*e*	0.5946(6)	0.0168(3)	0.2666(4)	0.027(2)	0.032(2)	0.034(1)	0.007(1)	0.009(1)	0.005(1)
C(1)	4*e*	0.7929(5)	–0.2152(2)	0.5724(3)	0.024(1)	0.029(2)	0.030(1)	0.002(1)	0.011(1)	0.003(1)
C(2)	4*e*	0.0205(6)	–0.3046(4)	0.6245(5)	0.029(2)	0.032(2)	0.063(2)	0.005(1)	0.013(2)	0.003(2)

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