Refinement of crystal structure of copper acetate diammine,
Cu(CH$_3$COO)$_2$·2NH$_3$

Harald Euler*1, Hartmut Kutzke1, Bruno Barbier1 and Armin Kirfel1

1 University of Bonn, Steinmann-Institute, Mineralogy, Poppelsdorfer Schloss, 53115 Bonn, Germany
2 University of Oslo, Museum of Cultural History, Postboks 6762, St. Olav's plass, 0130 Oslo, Norway

Received September 25, 2009, accepted and available on-line November 4, 2009; CCDC no. 1267/2783

Abstract

C$_4$H$_{12}$C$_{11}$N$_2$O$_4$, monoclinic, P12$_1$/c1 (no. 14), a = 5.452(2) Å, 
b = 10.220(5) Å, c = 7.518(5) Å, ß = 107.067(3)°, 
V = 400.5 Å$^3$, Z = 2, R$_{g}$F) = 0.032, wR$_2$) = 0.082, 
Γ = 295 K.

Source of material

A first structure determination of the title compound was re-
ported, based on intensities estimated from Weissenberg film ex-
posures [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 were 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 crystal-
lized 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$_g$/N$_{param}$ ratio.
Upon adjusting to the standard intensity decrease, the initial
internal agreement factor R$_2$) 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 Cl—Ol of 1.240(3) Å and
Cl—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 be-
tween Cl—Ol—O2 = 53.77(1)°, Cl—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 character-
ized 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(01—H1) = 2.23(4) Å, d(H1—N) = 0.77(4) Å,
d(O1—N) = 2.984(4) Å, d(N—H—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—H—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—H—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 disor-
der, which may be due to a torsional oscillation as suggested for
copper acetate monohydrate [6].

Table 1. Data collection and handling.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>blue plate, size 0.18 × 0.4 × 0.4 mm</td>
</tr>
<tr>
<td>Wavelength</td>
<td>Mo K$_\alpha$ radiation (0.71069 Å)</td>
</tr>
<tr>
<td>μ</td>
<td>26.98 cm$^{-1}$</td>
</tr>
<tr>
<td>Diff. mode</td>
<td>RIGAKU AFC-6R, ω</td>
</tr>
<tr>
<td>2θ max</td>
<td>50.1°</td>
</tr>
<tr>
<td>N(hkl) measured</td>
<td>11378, 714</td>
</tr>
<tr>
<td>N(hkl) unique</td>
<td>77</td>
</tr>
<tr>
<td>Criterion for I$_{obs}$</td>
<td>I$<em>{obs}$ &gt; 2σ(I$</em>{obs}$), 593</td>
</tr>
<tr>
<td>Programs</td>
<td>SHELXL-97 [8], SHELXL-97 [9], DIAMOND [10]</td>
</tr>
</tbody>
</table>

* Correspondence author (e-mail: H.Euler@uni-bonn.de)
Table 2. Atomic coordinates and displacement parameters (in Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₃</th>
<th>U₂₃</th>
<th>U₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>4e</td>
<td>0.526(6)</td>
<td>0.073(4)</td>
<td>0.202(4)</td>
<td>0.03(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(2)</td>
<td>4e</td>
<td>0.983(7)</td>
<td>-0.383(4)</td>
<td>0.603(5)</td>
<td>0.06(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(3)</td>
<td>4e</td>
<td>0.581(7)</td>
<td>-0.054(4)</td>
<td>0.203(5)</td>
<td>0.04(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(4)</td>
<td>4e</td>
<td>0.983(7)</td>
<td>-0.383(4)</td>
<td>0.603(5)</td>
<td>0.06(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(5)</td>
<td>4e</td>
<td>0.161(8)</td>
<td>-0.268(4)</td>
<td>0.577(5)</td>
<td>0.08(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(6)</td>
<td>4e</td>
<td>0.10(1)</td>
<td>-0.291(6)</td>
<td>0.752(8)</td>
<td>0.12(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Continued.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₃</th>
<th>U₂₃</th>
<th>U₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2d</td>
<td>½</td>
<td>0</td>
<td>½</td>
<td>0.0171(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>4e</td>
<td>0.5756(4)</td>
<td>-0.2589(2)</td>
<td>0.4947(3)</td>
<td>0.023(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>4e</td>
<td>0.8328(3)</td>
<td>-0.0939(2)</td>
<td>0.6105(2)</td>
<td>0.0212(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>4e</td>
<td>0.5946(6)</td>
<td>0.0168(3)</td>
<td>0.2666(4)</td>
<td>0.027(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>4e</td>
<td>0.7929(5)</td>
<td>-0.2152(2)</td>
<td>0.5724(3)</td>
<td>0.024(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>4e</td>
<td>0.0205(6)</td>
<td>-0.3046(4)</td>
<td>0.6245(5)</td>
<td>0.029(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References

5. van Niekerk, J. N.; Schoening, F. R. L.: A New Type of Copper Complex as found in the Crystal Structure of Cupric Acetate, Cu(CH₃COO)₂ · 2H₂O. Acta Crystallogr. 6 (1953) 227-232.