Crystal structure of trihydroxydicopper formate, \( \text{Cu}_2(\text{OH})_3(\text{HCOO}) \)

Harald Euler\(^1\), Bruno Barbier\(^1\), Armin Kirfel\(^1\), Stefanie Haseloff\(^{II}\) and Gerhard Eggert\(^{III}\)

\(^1\) Universität Bonn, Steinmann-Institut, Mineralogie, Poppelsdorfer Schloss, 53115 Bonn, Germany  
\(^{II}\) Universität Freiburg, Institut für Anorganische und Analytische Chemie, Lehrstuhl für Festkörperchemie, Alberstr. 21, 79104 Freiburg im Breisgau, Germany  
\(^{III}\) Staatliche Akademie der Bildenden Künste Stuttgart, Am Weißenhof 1, 70191 Stuttgart, Germany

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Abstract

\( \text{CH}_4\text{Cu}_2\text{O}_4 \), monoclinic, \( P12_11 \) (no. 4), \( a = 5.5894(2) \ \text{Å}, b = 6.0558(3) \ \text{Å}, c = 6.9321(3) \ \text{Å}, \beta = 105.926(2)^\circ \), \( V = 225.6 \ \text{Å}^3 \), \( Z = 2 \), \( R_{\text{W}(F)} = 0.038 \), \( wR_{\text{exp}}(F^2) = 0.121 \), \( T = 295 \ \text{K} \).

Source of material

Indoor museum air pollution by formaldehyde and formic acid (e.g., emitted from wood) may cause the formation of formates on historic objects made for example from limestone, glass, or lead [1]. Nevertheless, similar observations on copper alloys are limited only to cases where sodium salts are present [2]. To help with future identifications, Scott et al. [3] synthesized basic copper formates following the methods given by Fowles [4] and published their hitherto unknown powder diffraction data from Debye-Scherrer films. In a project to identify joint copper-glass corrosion compounds we found a diffraction pattern matching the film 770 on three corrosion samples from the contact zone of copper-containing alloys with sodium-containing glass: a 200 year old glass flute with silver mounting (Rijksmuseum Amsterdam), a silver-mounted ruby glass box (Green Vault Dresden), and an enamelled St. Matthew cross made from brass or bronze (MAK Frankfurt) [5]. Single crystals of this compound could be grown via Fowles method.

Experimental details

As a result of the crystal growth via the Fowles method, we obtained crystals of poor quality. According to the systematic extinctions \( 0k0, k = 2n+1 \), the possible space groups were \( P2_1 \) and \( P2_1/m \). The structure could only be solved in \( P2_1 \). First refinements indicated inversion twinning by the ratio 0.40(6)/0.60(6). Three of the 4 hydrogen atoms (H2, H3, H4) were found by Fourier mapping. Their coordinates as well as a common isotropic displacement parameter were refined. The position of H1 was calculated and kept fixed, contrary to its displacement parameter. The refinement converged at \( R_1 = 0.038, R_w = 0.121, \) GOOF = 1.086, Flack parameter \( x = 0.00(6) \). Upon structure inversion, only the twin ratio inverted to 0.60(6)/0.40(6). Thus, due to inversion twinning, the resonant scattering was not sufficient to allow for the determination of the absolute structure.

Discussion

The crystal structure is characterized by puckered layers, made of two different edge-sharing, Jahn-Teller distorted \( \text{CuO}_6 \) octahedra \( d(\text{Cu}1-O) = 1.931(1) \ - 2.408(8) \ \text{Å}, d(\text{Cu}2-O) = 1.970(9) - 2.389(2) \ \text{Å} \), oriented parallel to \( (001) \). The basal plane corners of the octahedron, centered by Cu1, are provided by the hydroxyl groups, whereas the apices are occupied by the single-bonded oxygen atoms of the formate groups. For the Cu2 octahedron, the apices are occupied by the oxygen atoms of the formate and hydroxyl groups. Alternating chains of Cu1 and Cu2 octahedra, running parallel \( [010] \), are connected to puckered layers by three common edges. Correspondingly, the Cu atoms of each layer form a nearly regular two-dimensional hexagonal packing as do oxygen atoms above and below each Cu layer. These most likely fairly stable \( \text{O} - \text{Cu} - \text{O} 'sandwiches' \) are held together by hydroxyl bonds between the hydroxyls of the formate groups and the oxygens of the formate groups \( d(O7\ldots H4) = 0.97(5) \ \text{Å} \), \( d(O7\ldots O5) = 2.690(3) \ \text{Å}, d(H4\ldots O5) = 1.96(6) \ \text{Å}, Z(07\ldots H4\ldots O5) = 130(5) \).

Table 1. Data collection and handling.

| Crystal: | blue prism, size 0.06 × 0.08 × 0.10 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 93.39 cm⁻¹ |
| Diffractometer, scan mode: | Bruker-AXS X8 APEXII, ϕ/ω |
| 2θmax: | 71.54° |
| N(hkl)measured, N(hkl)unique: | 12403, 1570 |
| Criterion for Iobs, I(hkl): | Iobs > 2σ(Iobs), 1140 |
| N(param)final: | 85 |
| Programs: | SHELXS-97 [6], SHELXL-97 [7], DIAMOND [8] |
### 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>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
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<tr>
<td>H(2)</td>
<td>2a</td>
<td>0.14(1)</td>
<td>0.29(1)</td>
<td>1.263(9)</td>
<td>0.07(1)</td>
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</table>

### Table 3. Atomic coordinates and displacement parameters (in Å²).

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<th>U₁₁</th>
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<tr>
<td>Cu(1)</td>
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<td>0.131(2)</td>
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<td>0.001(2)</td>
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<td>0.001(1)</td>
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### References