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Crystal structure of aqua-(5-nitrosalicylate-\(\kappa^2 O,O'\))-(1,10-phenanthroline-\(\kappa^2 N,N'\))copper(II), C\(_{19}\)H\(_{13}\)CuN\(_3\)O\(_6\)

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Abstract
C\(_{19}\)H\(_{13}\)CuN\(_3\)O\(_6\), monoclinic, \(P2_1/c\), \(a = 7.208(3)\) Å, \(b = 21.720(8)\) Å, \(c = 11.098(5)\) Å, \(\beta = 99.085(17)\)°, \(V = 1715.8(12)\) Å\(^3\), \(Z = 4\), \(R_{	ext{wp}}(F) = 0.0428\), \(wR_{	ext{ref}}(F^2) = 0.1044\), \(T = 293\) K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material
A mixture of Cu(NO\(_3\))\(_2\)-4H\(_2\)O (0.1 mmol), phenanthroline(phen) (0.1 mmol), 5-nitrosalicylic acid (0.2 mmol) and distilled water (10 mL) was added into a Teflon-lined autoclave (20 mL) and heated at 180°C for 72 h. Green chunk-like crystals of the title complex were collected from the reaction mixture.

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Table 1: Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal:</th>
<th>Green chunk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size:</td>
<td>0.36 × 0.18 × 0.12 mm</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>Mo Kα radiation (0.71073 Å)</td>
</tr>
<tr>
<td>(\mu):</td>
<td>13.2 cm(^{-1})</td>
</tr>
<tr>
<td>Diffraclometer, scan mode:</td>
<td>TeXan-PC, (\omega)</td>
</tr>
<tr>
<td>2(\theta)(_{\text{max}}), completeness:</td>
<td>55°, &gt;99%</td>
</tr>
<tr>
<td>(N(hkl))(<em>{\text{measured}}, N(hkl))(</em>{\text{unique}}, R(_{\text{int}}):</td>
<td>16553, 3944, 0.072</td>
</tr>
<tr>
<td>Criterion for (I_{\text{obs}}), (N(\text{hkl}))(_{\text{gt}}):</td>
<td>(I_{\text{obs}} &gt; 2\sigma(I_{\text{obs}}), 2401)</td>
</tr>
<tr>
<td>(N(\text{param}))(_{\text{refined}}):</td>
<td>268</td>
</tr>
<tr>
<td>Programs:</td>
<td>SHELX [6], TeXan-PC [7]</td>
</tr>
</tbody>
</table>

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\)).

<table>
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<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{	ext{iso}}/U_{	ext{eq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>0.32548(5)</td>
<td>0.686288(17)</td>
<td>0.07623(3)</td>
<td>0.03931(14)</td>
</tr>
<tr>
<td>N1</td>
<td>-0.1219(5)</td>
<td>0.47485(13)</td>
<td>-0.3285(3)</td>
<td>0.0609(9)</td>
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<tr>
<td>N2</td>
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<td>0.1188(2)</td>
<td>0.0385(6)</td>
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<tr>
<td>N3</td>
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<td>0.67276(12)</td>
<td>0.2312(2)</td>
<td>0.0414(6)</td>
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<tr>
<td>O1</td>
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<td>0.6959(1)</td>
<td>-0.25518(19)</td>
<td>0.0441(5)</td>
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<tr>
<td>O2</td>
<td>0.1849(3)</td>
<td>0.70907(9)</td>
<td>-0.07735(18)</td>
<td>0.0424(5)</td>
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<tr>
<td>O3</td>
<td>0.3215(3)</td>
<td>0.60067(10)</td>
<td>0.0427(2)</td>
<td>0.0497(6)</td>
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<tr>
<td>O4</td>
<td>-0.1081(4)</td>
<td>0.41922(11)</td>
<td>-0.3351(2)</td>
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<tr>
<td>O5</td>
<td>-0.2387(5)</td>
<td>0.50388(13)</td>
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<td>0.1158(15)</td>
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<td>O6</td>
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<td>0.60568(13)</td>
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<td>0.0352(7)</td>
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<td>O7</td>
<td>0.2176(4)</td>
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<td>0.0392(7)</td>
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<tr>
<td>O8</td>
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<td>0.50895(15)</td>
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<td>0.0471(8)</td>
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<tr>
<td>O9</td>
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<td>0.057*</td>
</tr>
<tr>
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<td>0.47613(14)</td>
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<tr>
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</tr>
<tr>
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<tr>
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<tr>
<td>O18</td>
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<td>0.0509(9)</td>
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<td>0.3223</td>
<td>0.9190</td>
<td>0.0603</td>
<td>0.061*</td>
</tr>
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<td>O20</td>
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<tr>
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<td>0.0519(9)</td>
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<tr>
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<td>0.8775</td>
<td>0.4382</td>
<td>0.062*</td>
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</table>
Table 2 (continued)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(U_{	ext{iso}}/U_{	ext{eq}})</th>
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</thead>
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<td>0.7238(5)</td>
<td>0.78801(19)</td>
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<td>0.0526(9)</td>
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<tr>
<td>H13A</td>
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<td>0.0377(7)</td>
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<td>0.6601(12)</td>
<td>0.234(3)</td>
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</tr>
</tbody>
</table>

Experimental details

The aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation \([C−H = 0.93 \text{ Å} \text{ and } U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(C)\]). The H atoms of the water ligand were found in a difference Fourier map and were refined with distance restraints of O−H = 0.83(1) Å and \(U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(O)\).

Discussion

Salicylic acid and its substituted derivatives continue to attract attention because of its versatile coordination modes and biological applications. Many complexes with salicylic acid derivatives and N-donor ligands were found to display diverse structure types [1–3]. Though the non-coordinating functional groups such as NO\(_2\), NH\(_2\), etc. are well known to form robust and strong hydrogen bonds, but metal-organic supramolecular assemblies employing organic ligands having NO\(_2\) groups are limited [4, 5]. In the crystal structure of the title complex, Cu atom adopts a square-pyramidal N\(_2\)O\(_3\) environment, with the basal plane defined by atoms O\(_1\) and O\(_3\) from one 5-(NO\(_2\))sal ligand and the atoms N2 and N3 from one phen ligand, and finally atom O6 from coordinated water occupying the apical position. The water ligand shows a long Cu1–O6 distance of 2.336(3) Å. The 5-(NO\(_2\))sal ligand is coordinated to Cu atom via one oxygen atom of the carboxylate group (O2) and one oxygen atom from the phenol group (O3). The carboxylate group of the 5-(NO\(_2\))sal ligand is approximately coplanar to the aromatic ring with a dihedral angle of 9.1(2)°. The adjacent mononuclear units are further connected to each other by O−H⋯O hydrogen bonds, resulting in extended 3D framework.

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References