**π-Complex of Cu(I) Chloride with 1-Allyloxybenzotriazole**

\[ \text{CuCl} \cdot \text{C}_6\text{H}_4\text{N}_3(\text{OC}_3\text{H}_5) \]

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Abstract—Single crystals of CuCl \(\cdot\) C\(_6\)H\(_4\)N\(_3\)(OC\(_3\)H\(_5\)) (I) are synthesized by ac electrochemical method from Cu(II) chloride and 1-allyloxybenzotriazole in ethanol solution and their unit cell parameters are determined: space group \(P2_1\)/\(a\), \(a = 11.583(4)\) \(\text{Å}\), \(b = 11.443(7)\) \(\text{Å}\), \(c = 8.620(4)\) \(\text{Å}\), \(β = 108.77(3)°\), \(V = 1082(2)\) \(\text{Å}^3\), \(R(F) = 0.0366\), \(R_w(F) = 0.0396\) for 1095 reflections. In the structure of \(\pi\)-complex I, inorganic fragment CuCl\(_2\) forms centrosymmetric parallelogram. A molecule of 1-allyloxybenzotriazole acts as a bridge, which is bonded to the Cu atoms of two inorganic dimers through the C=C bond of the allyl group and to the N atom of a triazole ring. Owing to this bridging function, the ligand molecules form zigzag organometallic layers. The trigonal-pyramidal coordination sphere of a metal atom includes two Cl atoms and the C=C group. The structural motif of complexes I significantly differs from that of the previously studied 2CuCl \(\cdot\) C\(_6\)H\(_4\)N\(_3\)(OC\(_3\)H\(_5\)) and resembles the motif of a bromide analog Cu\(_2\)Br\(_2\) \(\cdot\) [C\(_6\)H\(_4\)N\(_3\)(OC\(_3\)H\(_5\))]\(_2\).

The \(\pi\)-complexes of Cu(I) with 1-allylbenzotriazole CuCl \(\cdot\) C\(_6\)H\(_4\)N\(_3\)(C\(_2\)H\(_4\)) [1], with cations of 1,3-benzotriazolium [(C\(_6\)H\(_4\)N\(_3\))(C\(_2\)H\(_4\))]\(_2\)CuBr\(_2\) [2] and 1,3-benzimidazolium [(C\(_7\)H\(_6\)N\(_2\))(C\(_6\)H\(_4\))]\(_2\)CuCl\(_2\) and [(C\(_2\)H\(_4\)N\(_2\))(C\(_6\)H\(_4\))] \(\cdot\) Cu\(_3\)(Cl\(_{0.67}\)Br\(_{0.33}\)) [3, 4] have been recently synthesized and structurally studied. It was found that similar ligands, i.e., cations of 1,3-benzotriazolium and 1,3-benzimidazolium, form different crystal structures with the same Cu(I) salt. The indicated ligands act as bridges in the compounds under consideration, while 2-allylthiobenzimidazole performs chelate function in Cu(I) chloride and bromide complexes (1 : 1) [5]. Obviously, insignificant geometrical differences in the structures of the starting ligands can be the reason for different crystal structures of the complexes they form.

In continuation of the above-mentioned studies, we synthesized Cu(I) chloride and bromide complexes with 1-allyloxybenzotriazole of the composition 1 : 1 and 1 : 1 [6]. A new \(\pi\)-complex of Cu(I) chloride with 1-allyloxybenzotriazole CuCl \(\cdot\) C\(_6\)H\(_4\)N\(_3\)(OC\(_3\)H\(_5\)) (I) was obtained when the synthesis conditions were changed. The results of its X-ray diffraction analysis are reported in this paper.

EXPERIMENTAL

Synthesis. 1-Allyloxybenzotriazole was prepared by the procedure similar to that described in [7] from 1-oxybenzotriazole and allyl chloride in the presence of NaHCO\(_3\) in ethanol.

Compound I was synthesized by ac electrochemical method [8] from ethanol solution of CuCl\(_2\) \(\cdot\) 2H\(_2\)O (1 mmol) and 1-allyloxybenzotriazole (1.2 mmol) using ac current (50 Hz, 0.3 V). Single crystals of (I) with adequate quality were formed on copper electrodes in 48 h.

X-ray diffraction analysis. Crystals I were preliminarily studied by photomethod. The structure was solved using array of integrated intensities of reflections with \(I \geq 2\sigma(I)\) measured on automated DArCh diffractometer (MoK\(_\alpha\) radiation, \(λ = 0.71069\) Å, θ/2θ scan mode). The unit cell parameters refined by least-squares method with respect to adjustment angles of 24 reflections in a range of 25° \(\leq\) 2 ≤ 30°, and details of data collection for complex I are given in Table 1.

The structure of I was solved with CSD program package [9]. The positions of halogen atoms and of copper atom were determined by the direct methods, the remaining non-hydrogen atoms were localized from the Fourier synthesis. The positions of hydrogen atoms were established partially from the Fourier difference synthesis and partially from geometrical considerations. The coordinates and thermal parameters of non-hydrogen atoms were refined by least-squares method in anisotropic approximation. The coordinates and thermal parameters were refined for hydrogen atoms. The figures were obtained with DIAMOND software.

The coordinates and thermal parameters of atoms in structure I are listed in Table 2, the bond lengths and bond angles are given in Table 3.
RESULTS AND DISCUSSION

In the structure of compound I, the Cu and Cl atoms form centrosymmetric fragments Cu₂Cl₂, which were for the first time discovered in Cu(I) chloride π-complex with 1-allyl-3,5-dimethylpyrazole [11]. The 1-allyloxybenzotriazole molecule in complex I performs the bridging function and is bonded to the Cu atoms of two inorganic dimers through the C=C bond of the allyl group and to the N atom of triazole ring. The Cu₂Cl₂ fragment is bonded, in turn, with four ligand molecules, thus forming infinite double layers perpendicular to the x axis (Fig. 1). One can distinguish cyclic fragment [Cu₂Cl₂ · C₆H₄N₃(C₃H₅)]₄ in the layer (Fig. 2). Similar fragments [Cu₂Cl₂ · C₆H₄N₃(C₃H₅)]₃ were discovered in the structures of Cu(I) π-complexes C₆H₄N₃(C₃H₅)CuCl [1] and C₆H₄N₃(C₃H₅)CuCl₀.₈₄Br₀.₁₆ [6].

Table 1. Details of data collection and crystallographic data for compound I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Space group</td>
<td>P2₁/a</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.583(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>11.443(7)</td>
</tr>
<tr>
<td>c, Å</td>
<td>8.620(4)</td>
</tr>
<tr>
<td>β, deg</td>
<td>108.77(3)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>1082(2)</td>
</tr>
<tr>
<td>F(000)</td>
<td>552</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ(calcld.), g/cm³</td>
<td>1.683(3)</td>
</tr>
<tr>
<td>ρ(exp), g/cm³</td>
<td>1.7</td>
</tr>
<tr>
<td>Refinement method</td>
<td>F̃ijkl</td>
</tr>
<tr>
<td>Weighing scheme</td>
<td>[σ²(F) + 0.0020F₂an]⁻¹</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>0.0012(5)</td>
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<tr>
<td>Number of refined parameters</td>
<td>174</td>
</tr>
<tr>
<td>2θ, deg; sinθ/λ_max</td>
<td>50.02; 0.595</td>
</tr>
<tr>
<td>Number of measured reflections</td>
<td>1245</td>
</tr>
<tr>
<td>Refined reflections (I &gt; 2σ(I))</td>
<td>1095</td>
</tr>
<tr>
<td>R(F), R_w</td>
<td>0.0366, 0.0396</td>
</tr>
<tr>
<td>GOOF</td>
<td>1.010</td>
</tr>
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Table 2. Coordinates and thermal parameters* of atoms in compound I

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<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_eq/exp, Å²</th>
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<tr>
<td>Cu</td>
<td>0.89770(6)</td>
<td>0.10621(5)</td>
<td>0.95550(9)</td>
<td>4.74(3)</td>
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<tr>
<td>Cl</td>
<td>0.0580(1)</td>
<td>0.0977(1)</td>
<td>0.8653(2)</td>
<td>5.32(5)</td>
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<tr>
<td>N(1)</td>
<td>0.5824(4)</td>
<td>-0.0508(4)</td>
<td>0.7430(6)</td>
<td>5.0(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.6564(4)</td>
<td>0.0218(4)</td>
<td>0.8464(5)</td>
<td>4.8(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.8299(5)</td>
<td>0.1968(5)</td>
<td>0.1090(7)</td>
<td>5.3(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.9482(5)</td>
<td>0.2209(4)</td>
<td>0.1467(7)</td>
<td>5.0(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.5068(5)</td>
<td>-0.1703(5)</td>
<td>0.9069(7)</td>
<td>5.5(2)</td>
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<tr>
<td>C(4)</td>
<td>0.8027(5)</td>
<td>-0.0351(5)</td>
<td>0.5502(7)</td>
<td>5.7(2)</td>
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<tr>
<td>C(5)</td>
<td>0.7599(6)</td>
<td>-0.1080(5)</td>
<td>0.4204(7)</td>
<td>6.6(3)</td>
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<td>C(6)</td>
<td>0.6514(7)</td>
<td>-0.1710(6)</td>
<td>0.3918(8)</td>
<td>7.6(3)</td>
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<td>C(7)</td>
<td>0.5794(6)</td>
<td>-0.1595(5)</td>
<td>0.4870(8)</td>
<td>6.5(3)</td>
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<td>C(8)</td>
<td>0.6227(5)</td>
<td>-0.0845(4)</td>
<td>0.6181(7)</td>
<td>4.3(2)</td>
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<tr>
<td>C(9)</td>
<td>0.7318(4)</td>
<td>-0.0253(4)</td>
<td>0.6530(6)</td>
<td>4.3(2)</td>
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<tr>
<td>H(11)</td>
<td>0.791(6)</td>
<td>0.154(6)</td>
<td>0.160(8)</td>
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<tr>
<td>H(12)</td>
<td>0.762(4)</td>
<td>0.244(4)</td>
<td>0.046(6)</td>
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</tr>
<tr>
<td>H(21)</td>
<td>0.004(6)</td>
<td>0.176(6)</td>
<td>0.227(8)</td>
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<tr>
<td>H(31)</td>
<td>0.441(8)</td>
<td>-0.187(7)</td>
<td>0.970(11)</td>
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<tr>
<td>H(32)</td>
<td>0.418(6)</td>
<td>-0.203(6)</td>
<td>0.837(10)</td>
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</tr>
<tr>
<td>H(41)</td>
<td>0.880(4)</td>
<td>0.007(4)</td>
<td>0.573(5)</td>
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</tr>
<tr>
<td>H(51)</td>
<td>0.814(7)</td>
<td>-0.122(6)</td>
<td>0.359(10)</td>
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<tr>
<td>H(61)</td>
<td>0.623(7)</td>
<td>-0.211(7)</td>
<td>0.290(10)</td>
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<tr>
<td>H(71)</td>
<td>0.512(6)</td>
<td>-0.215(6)</td>
<td>0.475(9)</td>
<td></td>
</tr>
</tbody>
</table>

* B_eq/exp = 1/3ΣΣB_{ij}a_i^*a_j^*σ(α_α^*), for H atoms, the general thermal parameter B_{iso} = 8.2 Å².