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

CuCl · C₆H₄N₃(OC₃H₅)

E. A. Goreshnik* and M. G. Mys’kiv**

*Georg-August University, Goettingen, Germany
**Franko National University, ul. Kirilla i Mefodya 6, Lvov, 79005 Ukraine

Received June 22, 2004

Abstract—Single crystals of CuCl · C₆H₄N₃(OC₃H₅) (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 P2₁/a, a = 11.583(4) Å, b = 11.443(7) Å, c = 8.620(4) Å, β = 108.77(3)°, V = 1082(2) Å³, R(F) = 0.0366, Rω(F) = 0.0396 for 1095 reflections. In the structure of π-complex I, inorganic fragment Cu₂Cl₂ 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 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 π-complex of Cu(I) chloride with 1-allyloxybenzotriazole CuCl · C₆H₄N₃(OC₃H₅) (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-oxynbenzotriazole and allyl chloride in the presence of NaHCO₃ in ethanol.

Compound I was synthesized by ac electrochemical method [8] from ethanol solution of CuCl₂ · 2H₂O (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 ≥ 2σ(I) measured on automated DARCoh diffractometer (MoKα 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° ≤ 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(OC₃H₇)]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].