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CRYSTAL STRUCTURE OF AN $AgClO_4$ π COMPLEX WITH 2-AMINO-5-ALLYLTHIO-1,3,4-THIADIAZOLE OF THE COMPOSITION $[Ag(C_5H_7N_3S_2)(ClO_4)]$

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By interaction of $AgClO_4$ with 2-amino-5-allylthio-1,3,4-thiadiazole (Aatd) in the ethanol solution, a new $[Ag(Aatd)(ClO_4)]$ π complex is obtained. It is studied by single crystal X-ray diffraction.

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The 1,3,4-thiadiazole derivatives have a wide spectrum of properties promoting their use as biologically active substrates, phytohormones, optically active materials, and effective tools in crystal engineering of metal complexes [1-3]. Among the olefinic π complexes with transition metal ions containing a 1,3,4-thiadiazole core, about a dozen compounds have been structurally studied; five of them are Cu(I) π complexes with allyl derivatives of thiadiazole [4, 5]. With the aim to investigate the coordination capacities and behavior of allyl derivatives of 1,3,4-thiadiazole with respect to Ag^+, this communication reports the results of the synthesis and single crystal X-ray diffraction analysis of new π complex $[Ag(Aatd)(ClO_4)]$ (**1**) with 2-amino-5-allylthio-1,3,4-thiadiazole (Aatd).

Experimental. Synthesis. 5-Amino-1,3,4-thiadiazole-2-thiol was obtained by the known procedure [6] and its allyl derivative Aatd was obtained from 5-amino-1,3,4-thiadiazole-2-thiol and allyl chloride in the presence of $NaHCO_3$ in the ethanol solution. Yield was 92%.

The crystals of $[Ag(Aatd)(ClO_4)]$ compound (**1**) were synthesized by direct interaction of silver(I) perchlorate (formed *in situ* from Ag_2CO_3 and $HClO_4$) with Aatd in ethanol. To Aatd solution in ethanol at room temperature an equimolar amount of freshly prepared Ag_2CO_3 was added; the resulting suspension was acidified with concentrated $HClO_4$ to pH ~ 3. In two days, colorless crystals of compound **1** formed.

Single crystal X-ray diffraction. Integrated reflection intensities for the crystal of compound **1** were measured on a Kuma KM-4-CCD single crystal diffractometer (MoK_α radiation, graphite monochromator). The structure was solved and refined with the ShelXT and ShelXL software using the OLEX^2 interface [7, 8]. The details of the single crystal X-ray diffraction study and the main crystallographic data for **1** are as follows: composition $C_5H_7AgClN_3O_4S_2$, M = 380.58 g/mol, monoclinic crystals, space group $P2_1/c$, a = 9.517(3) Å, b = 7.900(3) Å, c = 14.752(4) Å, β = 102.79(3)°, V = 1081.6(6) Å^3, Z = 4, ρ_{calc} = 2.337 g/cm^3, μ(MoK_α) = 2.497 mm^{-1}, S = 1.053, $R(F)$ = 0.0557 for 2014 reflections with $I \geq 2\sigma(I)$, R_w = 0.1514 for all 2526 independent reflections. Atomic coordinates and other parameters of compound **1** have been deposited with the Cambridge Structural Database (No. CCDC 1495708) at www.ccdc.cam.ac.uk/data_request/cif.

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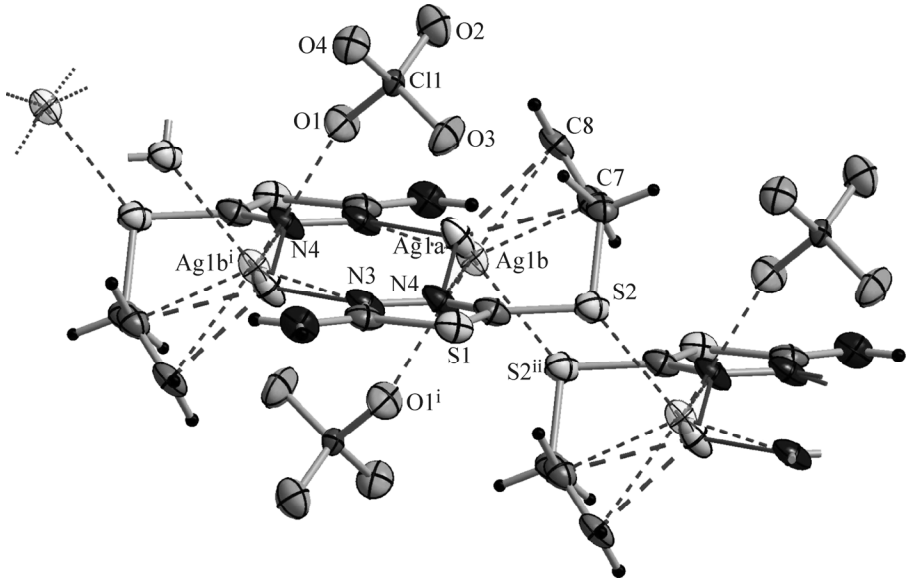

Fig. 1. Fragment of the structure of [Ag(Aatd)(ClO_4)] (**1**). Symmetry codes: ^{i} 1–*x*, 1–*y*, 1–*z*; ^{ii} 1–*x*, 2–*y*, 1–*z*.

Results and discussion. In the structure of **1**, the organic Aatd ligand molecule acts as a bridging chelate π,σ ligand and is coordinated to the Ag(I) atom by the olefinic C=C bond of the S-allyl group and by two (N3 and N4) atoms of the 1,3,4-thiadiazole core (Fig. 1). The silver(I) atom is disordered over two positions with the respective site occupancies of 0.76(3) (Ag1a) and 0.24(3) (Ag1b). An almost trigonal environment of Ag1a consists of the above mentioned active centers of the two neighboring Aatd molecules: the Ag1a–*m*^{i} (where *m* is the middle of the C=C bond, ^{i} 1–*x*, 1–*y*, 1–*z*), Ag1a–N4, and Ag1a–N3^{i} distances are, respectively, 2.337(5) Å, 2.267(5) Å, and 2.188(5) Å. Therefore, two nearest Ag1a atoms join two Aatd molecules into a centrosymmetric $\{[Ag(Aatd)]_2\}^{2+}$ dimer.

The coordination environment of the Ag1b atom increases to five due to the formation of two additional bonds: Ag1b–O1 (2.956(5) Å) with an oxygen atom of the perchlorate anion and Ag1b–S2^{ii} (3.002(5) Å, ^{ii} 1– *x*, 2–*y*, 1–*z*) with the sulfur atom of the allylthiol group of the neighboring $\{[Ag(Aatd)]_2\}^{2+}$ dimer. Both Ag1b–O1 and Ag1b–S2 distances are far less than the sum of the van der Waals radii of the respective atoms [9]. The Ag1b–*m*^{i}, Ag1b–N4, and Ag1b–N3^{i} distances are, respectively, 2.35(1) Å, 2.344(9) Å, and 2.36(1) Å.

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