Unexpected complexation of allylpseudothiohydantoin hydrochlorides towards Cu*X* (*X*=Cl, NO_3, ClO_4, BF_4, 1/2SiF_6). The first known examples of joint Cu^{I}(Cl,ClO_4) and Cu^{I}(Cl,BF_4) π-complexes.

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Streszczenie

By means of alternating current-electrochemical synthesis starting from a mixture of 2-imino-3-(prop-2-en-1-yl)-1,3-thiazolidin-4-one (3-allylpseudothiohydantoin, napt) and 2-allylamino-1,3-thiazol-4(5H)-one (allylaminopseudothiohydantoin, aapt) hydrochlorides and corresponding copper(II) salts five new π-complexes, [Cu(napt)Cl] (1), [Cu2(aapt)2Cl]NO3 (2), [Cu2(aapt)2Cl]BF4 (3), [Cu2(aapt)2Cl]ClO4 (4) and [Cu2(aapt)2Cl]2SiF6·2H2O (5), were obtained and studied by X-ray single crystal diffraction and IR-spectroscopy. Napt and aapt molecules are selectively coordinated to Cu+ depending on the anion type. In crystals of 1 and 5, the organic ligands are attached to the metal in a chelating N,(C=C)-bidentate mode. The aapt molecule in 2-4 acts as a tridentate chelating ligand, being coordinated to the copper(I) ion through the heterocyclic N atom, carbonyl O atom, and C=C bond of allyl group, forming an original cationic [Cu2(aapt)2Cl]+ fragment with both a bridging Cl– ion and O atom of the C=O group. In the presence of the doubly charged SiF62– anion, Cu(I) in 5 prefers to be bonded with two bridging Cl– ions, rather than the C=O group, causing [Cu2(aapt)2Cl]+ units to associate into the infinite cationic chains. Crystals of 3 and 4 are the first known examples of the simultaneous BF4–/Cl– or ClO4–/Cl– participation in copper(I) π-complex formation.

Słowa kluczowe

copper(I), π-complex, pseudothiohydantoin, heteroanionic, crystal structure

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