Formation of Cu\(^{(1)}\)(CH\(_3\)CN)\(_4\)ClO\(_4\) in the Reactions of Copper(II) Perchlorate with Acetonitrile in the Presence of Sulfur-Containing Organic Compounds


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Abstract—Cu(ClO\(_4\))\(_2\)·6H\(_2\)O was shown to react with 2,2'-[propane-1,3-diylbis(thio-2-phenylnemethylidene)]-bis(3-pyridylamine) (I) or (5Z)-2-ethoxycarbonylmethyl-(2-pyridylmethylidene)-3,5-dihydro-4\(\text{H}\)-imidazol-4-one (II) in the presence of CH\(_3\)CN with the reduction of copper(II) to copper(I) and the formation of the tetrahedral complex Cu\(^{(1)}\)(CH\(_3\)CN)\(_4\)ClO\(_4\) (III). In the course of the reaction the organic ligands I and II were oxidized to the corresponding sulfoxides.

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Spontaneous reduction of copper(II) during complexation with organic ligands is described in a series of papers [1–12]. In most cases the question which compound acted as a donor of electrons was not discussed, although in some papers the suggestions were made of participation of the solvent in the redox process or of occurrence of a photochemical reaction (see, for example, [6, 9]). On the other hand, in some cases the spontaneous reduction of the metal ion cannot be explained invoking only these factors, for example, when using the solvents incapable of oxidation [5, 6]. In these cases, it is reasonable to assume that the organic ligand used acts as a reducing agent.

Several examples were published of the formation of copper(I) complexes upon interaction of copper(II) salts with organic sulfides, containing, as a rule, additional nitrogen donor atoms and representing tetradentate ligands (see references above). In most cases, the oxidation product was not isolated but it might be assumed that during the reaction the one-electron oxidation of the thioether group by the Cu(II) ion occurred with the formation of the sulfur-centered radical-cation, which is further oxidized (by the air oxygen) or hydrolyzed to sulfoxide. Note that although under conventional conditions free sulfides are very slowly oxidized by the air oxygen, such a process catalyzed by the copper salts was described for oxidation of sulfur-containing macrocycles [13]. It is also noteworthy that in active centers of the most of mononuclear [14, 15] and binuclear [16] copper-containing enzymes the metal atom is coordinated just by the donor sulfur atoms (thioether or thiolate) and nitrogen atoms (usually imidazole). Such copper-containing enzymes (hemocyanins, thyrosinases, etc.) are capable to react with oxygen [17] and in the course of the reaction the exchange of electrons between the copper ion and the ligand occurs. Since sulfur itself is a soft donor, in a number of cases its coordination with soft Cu(I) turns out to be preferable as compared to coordination with more hard Cu(II); therefore the exchange of electrons between the metal and the ligand occurs in the complex.

When investigating the reactions of complexing of sulfur-containing organic ligands with copper(II) perchlorate in the presence of acetonitrile we have found that the main product of the reaction of compounds I and II (see scheme below) with Cu(ClO\(_4\))\(_2\)·6H\(_2\)O was the tetrahedral copper(I) complex Cu(CH\(_3\)CN)\(_4\)ClO\(_4\) (III) earlier characterized by X-ray structural analysis [18, 19].

1Dedicated to academician B.A. Trofimov on the occasion of his 70th birthday.
In the present work we tried to formulate the factors that make the reduction of copper(II) to copper(I) the predominant process in the complexing with organic ligands. Based on our data and those available from the literature, the structural criteria making the ligand capable of reducing copper(II) to copper(I) during complexing can be suggested.

We have found that complex III was the major product of the reaction of ligands I or II with copper(II) perchlorate at room temperature.

Upon mixing the solutions of copper(II) perchlorate and ligand I or II complex III was formed as colorless crystals whose structure was proved by X-ray analysis. The complex is stable in solution and in crystalline form in the absence of air, but gradually decomposes turning green when stored in air.

With this, the organic ligand suffers oxidation at the sulfur atom to the corresponding sulfoxide and hydrolysis, perhaps, catalyzed by the copper salt and, apparently, occurring by the action of the crystal-