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Formation of $Cu^{I}(CH_3CN)_4ClO_4$ in the Reactions of Copper(II) Perchlorate with Acetonitrile in the Presence of Sulfur-Containing Organic Compounds[1]

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Abstract—$Cu(ClO_4)_2 \cdot 6H_2O$ 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*H*-imidazol-4-one (**II**) in the presence of CH_3CN with the reduction of copper(II) to copper(I) and the formation of the tetrahedral complex $Cu^{I}(CH_3CN)_4ClO_4$ **(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 oxydized 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 $Cu(ClO_4)_2 \cdot 6H_2O$ was the tetrahedral copper(I) complex $Cu(CH_3CN)_4ClO_4$ (**III**) earlier characterized by X-ray structural analysis [18, 19].

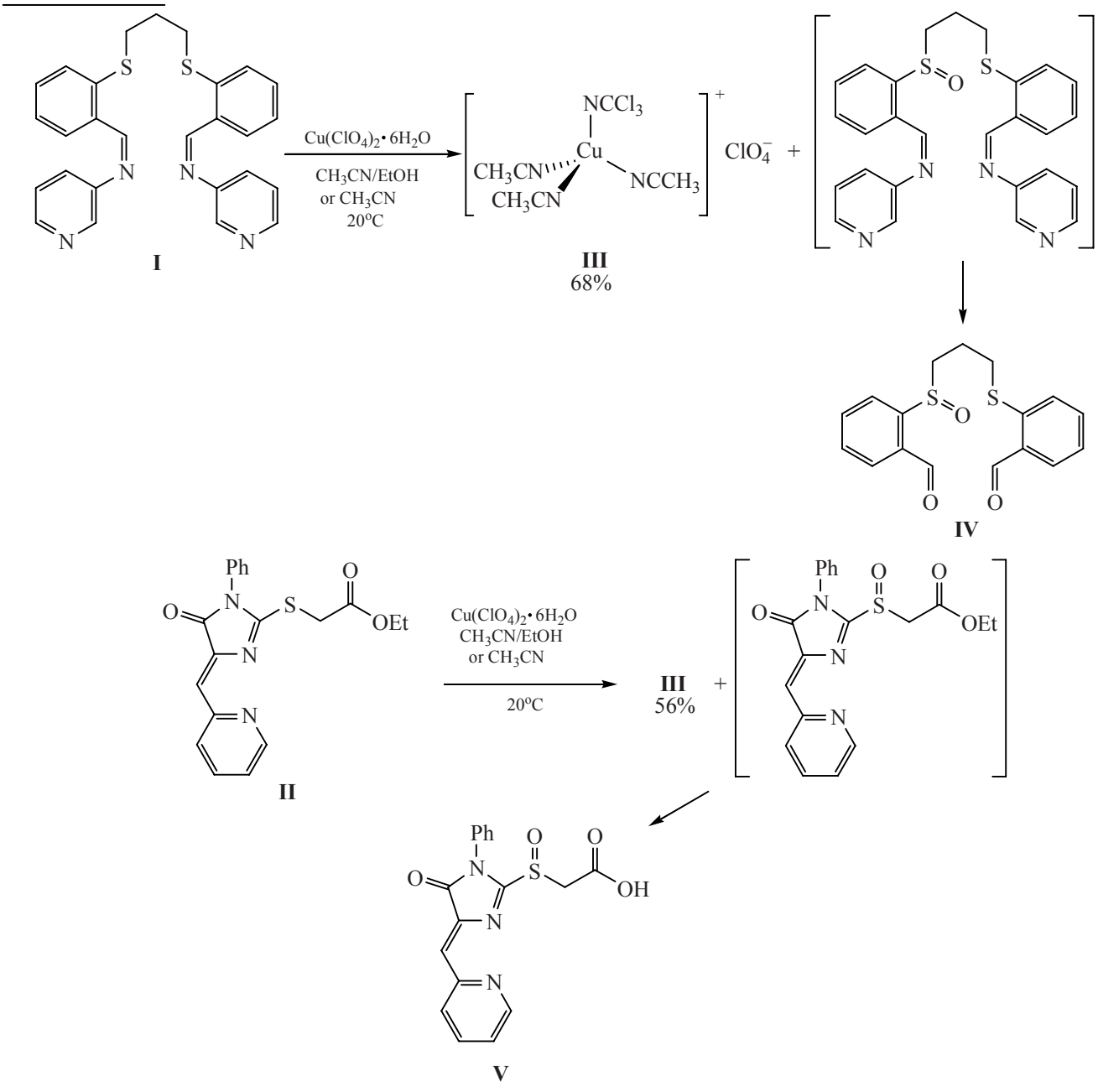
[1] Dedicated to academician B.A. Trofimov on the occasion of his 70th birthday.

In the present work we tried to formulate the factors that make the reduction of copper(II) to copper(I) the predominat 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 orhanic 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-



lization water present in the starting copper salt. As organic products of the reaction, we have isolated dialdehyde **IV** and acid **V**, respectively.

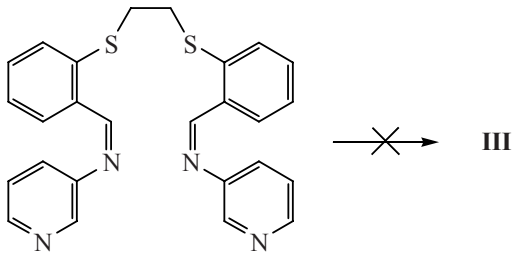
Note that we have for the first time observed the redox reaction during complexing copper(II) salt with bidentate organic ligand. This refutes the conclusion made in [7] that the presence of the tetradentate macrocyclic ligand is necessary for the reduction process $Cu^{II} \rightarrow Cu^{I}$ to occur. We succeeded in showing that the process of this type could proceed upon the interaction not only with acyclic but even with a bidentate ligand.

It is noteworthy that when copper(II) chloride is introduced in the reaction instead of the corresponding perchlorate, complex **III** is not formed. Apparently, this is due to the fact that chloride ion, as a strong electron-donor, coordinates directly with the copper ion, whereas non-nucleophilic perchlorate ion locates on the outer sphere of the complex. This is consistent with the preferred coordination of the soft copper(I) atom with soft sulfur atom of the thioether ligand, whereas the hard copper(II) atom is preferred for coordination with hard donor, chloride anion.

Apart from the counterion in the employed copper(II) salt, the possibility of spontaneous reduction of the metal ion during the reaction of complexing must be to a large extent determined by the used organic ligand. Several structural requirements to the ligand capable of being a donor in such a reaction can be formulated. Three factors should be taken into account:

(1) Correlation between the geometry of the complex and the copper ion oxidation state. For Cu(I) complexes (d^{10}) the tetrahedral or trigonal coordination is preferable, while for Cu(II) complexes (d^{9}) more typical is the octahedral, trigonal bypyramidal, square planar or tetrahedral geometry [20, 21].

On this basis, it should be assumed that to favor the $Cu^{II} \rightarrow Cu^{I}$ transition during the process of complexing, the ligand must not be conformationally rigid and the coordination surrounding of the copper ion could become tetrahedral. An indirect confirmation of this assumption is the fact that the reduction of copper(II) to copper(I), similar to that we observed, occurs in complexing with conformationally flexible macrocyclic ligands [4]. The assumption is also corroborated by the fact that ligand **IV** containing between the sulfur atoms a shorter bridge consisting of two carbon atoms does not give complex **III** when introduced in the reaction under conditions similar to those for the reaction "**I** + $Cu(ClO_4)_2 \cdot 6H_2O$:"



IV **III**

Note also that in natural mononuclear copper-containing enzymes (for example, plastocyanin [14] and azurine [15]) the active center containing two imidazole, thiolate and thioether donor atoms, can easily change its geometry, and in the form that stabilizes Cu(I) the coordination surrounding of copper represents a distorted tetrahedron.

(2) HSAB princile. Harder ligands (that is, charged, or containing the donor nitrogen or oxygen atoms rather than sulfur atoms) must better stabilize the hard Cu(II) cation. Soft uncharged sulfide ligands must better stabilize the soft Cu(I) cation.

This assumption is proved by investigation of complexing reactions with conformationally flexible ligands of similar structure differing only by the type of the donor system (N_4 or N_2S_2); the process of reduction $Cu^{II} \rightarrow Cu^{I}$ occurred only in the case of the N_2S_2 ligands, while for the ligands of the N_4 type the Cu(II) complex was formed [5].

(3) Donor ability of the ligand. Strong electron-donor ligands must stabilize higher oxidation state of the central metal atom [in our case, Cu(II)], whereas weakly donating or π-acceptor ligands (such as sulfides or nitriles) preferably stabilize a lower oxidation state [Cu(I)].

To summarize, it can be assumed that upon complexing of copper(II) salts with organic ligands, the formation of copper(I) complexes can be anticipa-

ted in the cases when organic reagent has the following structural features. (1) Bidentate ligand or tetradentate ligand with conformational flexibility sufficient for making the coordination surrounding of the copper ion tetrahedral. (2) The presence of a soft sulfide donor atom in the ligand. (3) Non-nucleophilic counterion in the starting inorganic salt.

Besides, in the reactions we studied, it turned out that it is necessary to use a nitrile-containing solvent (MeCN; when carrying out the reaction in EtOH the Cu(II) complexes are formed [22]). This can be understood since in the course of the redox reaction the sulfide group of the ligand oxidizes to the sulfoxide group (evidently, the source of the oxygen atom is the air oxygen since no formation of **III** is observed when performing the reaction in an argon atmosphere); the arising donor atom S(IV) is harder than the initial S(II) atom, and, therefore, apparently it is less strongly bound to the soft Cu(I) atom and is substituted in the coordination sphere by the soft nitrile ligand.

Based on the data obtained and available in the literature it can be assumed that it is the ligand that acts as a source of electrons for the metal ion reduction. These reactions simulate one of the studies of the process of electron transfer in copper-containing enzymes, where the ligand acts as a mediator of electron transfer from molecular oxygen. Electron transfer from ligand to metal requires a decrease in the energy of the transition state for the $Cu^{II} \rightarrow Cu^{I}$ process, which is possible on the condition of conformational flexibility and softness of the ligand.

EXPERIMENTAL

The reactions were monitored and the individuality of the products was checked by the method of thin layer chromatography on the fixed silica gel (Silufol). ^{1}H NMR spectra were registered on a Varian-XR-400 instrument with working frequency 400 MHz in $CDCl_3$. IR spectra were recorded on a UR-20 instrument in thin film or mineral oil. Electron impact mass spectra were registered on a JMS-D300 mass spectrometer (direct injection, ion source temperature 150ºC, energy of ionizing electrons 70 eV, accelerating voltage 3 kV).

Light-green crystals of compound **III** were analyzed on an automatic single-crystal diffractometer CAD-4 (κ, MoK_α = 0.71073, graphite monochromator, ω-scanning). Parameters of the unit cell were determined and refined from 25 reflections for angles in the range 14–16°: a = 24.223(3), b = 8.442(3), c = 20.716(1) Å, V = 4236.2(2), space group Pna2i, Z = 12. Correction for extinction was made by the use of ω-scanning [23]. The massive of experimental data was treated by the use of the package of programs WinGX [24]. All further calculations were performed using the SHELX97 program package [25]. The crystal structure was determined by the direct method with subsequent refinement of positional and thermal parameters for all non-hydrogen atoms by a full-matrix least-squares method in the anisotropic approximation. Hydrogen atoms were placed in the geometrically calculated positions by the use of the *rider* model. Final R factor = 0.0056 from 2624 reflections with intensity $I > 2a(I)$.

2,2'-[Propane-1,3-diylbis(thio-2-phenylnemethyl-idene]bis(3-pyridylamine) (I). In 15 ml of EtOH 948 mg (3 mmol) of 1,5-bis(2-formylphenyl)-1,5-dithiapentane and 564 mg (6 mmol) of 3-aminopyridine was dissolved, refluxed for 15 h, filtered, and the solvent was removed to obtain 980 mg (2.1 mmol, 70%) of brown oil. ^{1}H NMR ($CDC1_3$): 9.02, 9.01 s (2H), 8.49 m (4H), 8.12 m (2H), 7.50 m (2H) 7.34 m (8H), 3.03, 3.02 t (4H, J 7.0 Hz), 1.93 m (2H). IR spectrum (film): 1680, 1620, 1590, 1580, 1445, 1420. MS EI (*m/z*, %): 467 ($M–H^+$, 2.5).

5-Pyridylmethylidene-3-phenyl-2-carbethoxy-methylthiotetrahydro-4*H*-imidazol-4-one (II). To 0.3 g (1 mmol) of 3-phenyl-5(7)-2-pyridylmethyl-idene)-2-thioxotetrahydro-4*H*-imidazol-4-one 10 ml of water, 10 ml of ethanol, and 15% aqueous solution of KOH (0.063 g, 1 mmol) was added. After complete dissolution, 0.178 g (1 mmol) of ethyl bromoacetate was added and stirred for 3 h. The precipitate formed was filtered off, washed with ethanol, diethyl ether and dried in the air to obtain 0.364 g (93%) of compound **II**. ^{1}H NMR ($CDC1_3$): 8.81 d (1H J 7.8 Hz), 8.71 d (1H, J 4.0), 7.80 d. t (1H, J 7.7, 1.5 Hz), 7.45 m (4H), 7.28 m (3H), 4.28 q (2H, J 7.0, CH_2), 4.10 s (2H, CH_2), 1.31 t (3H, CH_3, J 7.0 Hz). Found, %: C 62.01; H 4.32; N 11.63. $C_{19}H_{17}N_3SO_3$. Calculated, %: C 62.11; H 4.66; N 11.44.

Reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with ligand I. 103 mg (0.22 mmol) of compound **I** and 81.4 mg (0.22 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ was refluxed in 2 ml of the mixture ethanol–acetonitrile (1:1) or CH_3CN in the course of 1 h, cooled to 0°C, the precipitated crystals (36 mg, yield 50%) were filtered off. IR spectrum (film, ν, cm^{-1}): 1680, 1645, 1625, 1590, 1565 (C=N). Found, %: C 28.67, H 3.43, N 15.80. $C_8H_{12}N_4CuClO_4$. Calculated,

%: C 29.36; H 3.67; N 17.13. After the mother liquor was cooled to –20°C 38 mg (55%) of compound **IV** was crystallized. ^{1}H NMR ($CDC1_3$): 10.20, 10.15 s (2H, CHO), 7.86 m (4H), 7.52 m (2H), 7.40 m (2H) 7.33 m (8H), 3.10, 3.12 t (4H, *J* 7.0 Hz), 2.11 m (2H). IR spectrum (vaseline oil, ν, cm^{-1}): 1700, 1650, 1210, 1065 (S=O). Found, %: C 64.84; H 5.02. $C_{17}H_{16}S_2O_2$. Calculated, %: C 64.56; H 5.06.

Reaction of $Cu(ClO_4)_2·6H_2O$ with ligand II. To the solution of 52 mg (0.14 mmol) of compound **II** in 2 ml of CH_2Cl_2 3 ml of CH_3CN was added for layer separation. Then the solution of 50 mg (0.14 mmol) of $Cu(ClO_4)_2·6H_2O$ in 2 ml of CH_3CN was slowly added. The reaction mixture was firmly closed and allowed to stay until the crystalline precipitate formed. The precipitate was filtered off, the solution filtered through the column with silica gel of 4–5 cm height. Solvent was removed, the obtained green oil was purified by TLC (eluent ethyl acetate:methanol 2:1) to obtain 11 mg (23%) of compound **V** as a white crystalline compound. IR spectrum (mineral oil): 3450 br, 1740, 1715, 1635, 1185, 995 (S=O). Found, %: C 56.38; H 4.02; N, 11.35. $C_{17}H_{13}N_3SO_4$. Calculated, %: C 57.46; H 3.66; N 11.83.

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REFERENCES

1. Schilstra, M.J., Birker, W.L., Verschoor, G.C., and Reedijk, J., *Inorg. Chem.*, 1982, vol. 21, p. 2637.
2. Olmstead, M.M., Musker, W.K., Kessler, R.M., *Inorg.Chem*., 1981, vol. 20, p.151.
3. Birker, W.L., Helder, J., Henkel, G., Krebs, B., and Reedijk, J., *Inorg. Chem*., 1982, vol. 21, p. 357.
4. Nanda, K.K., Addison, A.W., Butcher, R.J., McDevitt, M.R., Rao, T.N., and Sinn, E., *Inorg. Chem*., 1997, vol. 36, p. 134.
5. Malachowski, M.M., Adams, M., Elia, N., Rheingold, A.L., and Kelly, R.S., *J. Chem. Soc, Dalton Trans.,* 1999, p. 2177.
6. Benzekri, A., Cartier, C., Latour, J.-M., Limosin, D., Rey, P., and Verdaguer, M., *Inorg. Chim. Acta*, 1996, vol. 252, p. 413.
7. Nickless, D.E., Powers, M.J., and Urbach, F.L., *Inorg. Chem*., 1983, vol. 22, p. 3210.
8. Latour, J.M., Limosin, D., and Rey, P., J. *Chem. Soc, Chem. Commun*., 1985, p. 464.
9. Verheijdt, P.I., Hassnoot, J.G., and Reedijk, J., *Inorg. Chim. Acta*, 1983, vol. 76, p. L43.
10. Mandal, S.K., Woon, T.C., Tompson, L.K., Newlands, M.J., and Gage, E.J., *Aust. J. Chem*., 1986, vol. 39, p. 1007.
11. Kitawara, U.S., Munakata, M., and Higashi, A., *Inorg. Chim. Acta*, 1984, vol. 84, p. 79.
12. Sakurai, T., Kimura, M., and Nakahara, A., *Bull. Chem. Soc. Jpn*, 1981, vol. 54, p. 2976.
13. Musker, W.K., *Acc. Chem. Res*., 1980, vol. 13, p. 1040.
14. Colman, P.M., Freeman, H.C., Guss, J.M., Murata, M., Norris, V.A., Ramshaw, J.A.M., and Venkatappa, M.P., *Nature*, 1978, vol. 272, p. 319.
15. Adman, E.T., Stenkamp, R.E., Sieker, L.C., and Jensen, L.H., *J. Mol. Biol*., 1978, vol. 123, p. 35.
16. Latour, J.M., *Bull. Soc. Chim. France*, 1988, p. 508.
17. Sorrell, T.N. and Cheesman, E.H., *Synth. Commun*., 1981, vol. 11, p. 909.
18. Hemmerich, P. and Sigwart, G., *Experientia*, 1963, vol. 12, p. 488.
19. Soregh, C., Kierkegaard, P., and Norrestam, R., *Acta Cryst., Sect. B*., 1975, vol. 31, p. 314.
20. Bowmaker, G.A., Gill, D.S., Skelton, B.W., Somers, N., and White, A.H., *Z. Naturforsh, B: Chem*., 2004, vol. 59, p. 1307.
21. Cotton, F. and Wilkinson, G., *Sovremennaya neorganicheskaya khimiya* (Modern Inorganic Chemistry), vol. 3, Moscow: Mir, 1969.
22. Beloglazkina, E.K., Shimorsky, A.V., Majouga, A.G., Moiseeva, A.A., and Zyk, N.V., *Izv. Akad. Nauk., Ser. Khim.,* 2007, vol. 56, no. 11, p. 2189.
23. North, A.C.T., Philips, D.C., and Mathews, F.S., *Acta Cryst. A*, 1968, vol. 24, p. 351
24. Farrugia, L.A., *WinGX. X-Ray Crystallographic Programs for Window*, University of Glasgow, Glasgow, UK, 2003.
25. Sheldrick, G.M., *SHELX97. Program for the Solution and Refinement of Crystal Structures*, University of Gottingen, Gottingen, Germany, 1997.