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Mild Template Synthesis of (2,8-Dithio-3,7-diaza-4,6-dimethyl-5-oxanonanedithioamido-1,9)copper(II) in $Cu_2[Fe(CN)_6]$ Gelatin-Immobilized Matrices

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Abstract—Complexation process in $Cu_2[(Fe(CN)_6]$ gelatin-immobilized matrices in contact with aqueous solutions of dithiooxamide $H_2N–C(S)–C(S)–NH_2$ and ethanal $H_3C–CHO$ at pH > 10 were studied. The template synthesis was shown to occur under these specific conditions to yield the Cu(II) chelate with tetradentate (N,N,S,S)-ligand (2,8-dithio-3,7-diaza-4,6-dimethyl-5-oxanonanedithioamide-1,9) with a metal : ligand ratio of 1 : 1. Dithiooxamide and ethanal therein act as ligand syntones. The reaction scheme was suggested. It was established that this tetradentate ligand is not formed in the absence of Cu(II) in a solution in contact with the matrix. Moreover, the attempts made to obtain the title compound through the reactions of known copper(II) dithiooxamide complexes with ethanal failed.

Previously [1, 2], we established that template synthesis can be carried out under specific conditions, i.e., in a copper(II) hexacyanoferrate gelatin-immobilized matrix in contact with Cu(II)–dithiooxamide ($H_2N–CS–CS–NH_2$)–formaldehyde or Cu(II)–dithiooxamide–glyoxal systems. Organic components of these systems act therein as specific “building blocks” (so-called ligand syntones) for the formation of macrocyclic metal compounds. Another oxygen-containing compound capable of acting as a ligand syntone is ethanal Me–CHO (Me = methyl). The Cu(II)–dithiooxamide–ethanal system is a suitable object for use in verifying this suggestion. In this work, template synthesis occurring upon complexation in the $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrix was studied.

EXPERIMENTAL

The $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrices were synthesized by the procedure described in [1, 2]. The matrices obtained were brought in contact with aqueous solutions containing dithiooxamide (H_2L) at a concentration of 2.0×10^{-3}–2.0×10^{-1} mol/l and ethanal (Etl) at a molar ratio of 0.5–2.0 (pH 12.0 ± 0.1). The matrix was left in contact with a solution for 1–10 min at 20.0 ± 0.1°C. The procedure of the experiment and equipment used were as those described in [1, 2]. Kinetic curves $D^{\blacktriangledown} = f(c_{Fe}, c_{H_2L}, \tau)$ ($D^{\blacktriangledown}$ is the optical density of the metal-chelate matrix, c_{Fe} (mol/dm^3) is the initial concentration of copper(II) hexacyanoferrate(II) in the matrix, c_{H_2L} (mol/l) is the concentration of dithiooxamide in a solution, and τ (min) is the time of contact between the matrix and solution) are shown in Figs. 1 and 2, and the electronic absorption spectra of gelatin-immobilized matrices are presented in Fig. 3.

RESULTS AND DISCUSSION

When alkaline solutions containing dithiooxamide and ethanal ($c_{H_2L} < 10^{-5}$ mol/l, dithiooxamide : ethanal molar ratio 0.5–2.0) react with $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrices for a relatively long time ($\tau > 6$ min), the initial reddish-brown color of the matrix turns grayish-blue at all concentrations of $Cu_2[Fe(CN)_6]$ due to the formation of $[Cu(OH)_2]_n$ compound (**I**). The electronic absorption spectra of gelatin-immobilized matrices containing this compound exhibit a flattened band with λ_{max} = 680–700 nm in the visible range and coincide with the spectra of the gelatin-immobilized polymeric hydroxo complex $[Cu(OH)_2]_n$. After these matrices were destroyed, a grayish-blue polymeric copper(II) hydroxide was isolated, as determined from the elemental analysis data.

For $(H_2CuO_2)_n$			
anal. calcd. (%):	Cu, 65.31;	H, 2.04;	O, 33.61.
Found (%):	Cu, 64.7;	H, 2.1;	O, 33.2.

Mathematical analysis of the kinetic curves $D^{\blacktriangledown} = f(c_{Fe}, c_{H_2L}, \tau)$ using the procedure described in [3] indicated that neither dithiooxamide nor ethanal molecules were added in the studied concentration–time ranges but two hydroxo anions were added per copper(II) ion. This fact is evidence that, before complexation, copper(II) hexacyanoferrate(II) transforms into polymeric

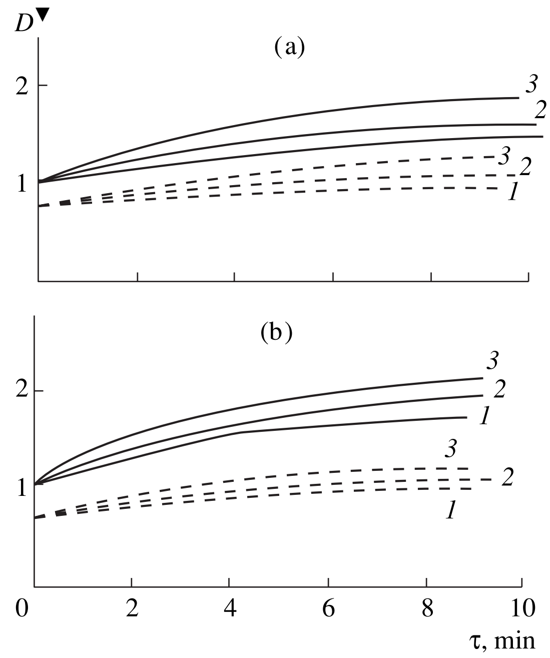


Fig. 1. $D^{\blacktriangledown}$ vs τ for the Cu(II)–H_2L–Etl system at c_{H_2L} = (*1*) 3.0×10^{-3}, (*2*) 6.5×10^{-3}, and (*3*) 1.2×10^{-2} mol/l; c_{Fe} = (– – –) 0.70 and (—) 1.00 mol/dm^3; H_2L : Etl molar ratio (a) 0.50 and (b) 1.0. λ_{max} = 450 nm.

Cu(II) hydroxide:

$$nCu_2[Fe(CN)_6] + 4nOH^-$$
$$\longrightarrow 2[Cu(OH)_2]_n + n[Fe(CN)_6]^{4-},$$

which is the starting form for further transformations. We observed similar phenomenon during complexation in $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrices in contact with C(II)–(N,S)-donor-chelating ligand systems, in particular, Cu(II)–dithiooxamide [4], Cu(II)–N,N'–diphenylthiooxamide [5], and Cu(II)–8-mercaptoquinoline [6].

At c_{Fe} = 0.1–1.0, $c_{H_2L} > 5.0 \times 10^{-2}$ mol dm^{-3}, τ = 2–10 min, and at a dithiooxamide : ethanal molar ratio exceeding 2.0, a compound **II** that turns the gelatin layer dark green is formed in the system studied. The spectral parameters of **II** agree with those of the coordination compound $[Cu(HL)_2]_n$ (H_2L—dithiooxamide) reported in [4]. After gelatin-immobilized matrices containing compound **II** were destroyed, a dark green substance whose empirical formula $CuC_4S_4N_4H_6$ corresponds to the $[Cu(HL)_2]_n$ complex was isolated.

For $CuC_4S_4N_4H_6$
anal. calcd.
(%): C, 15.89; H, 1.98; N, 18.55; Cu, 21.19; S, 42.39.
Found (%): C, 15.7; H, 2.3; N, 18.5; Cu, 20.9; S, 42.1.

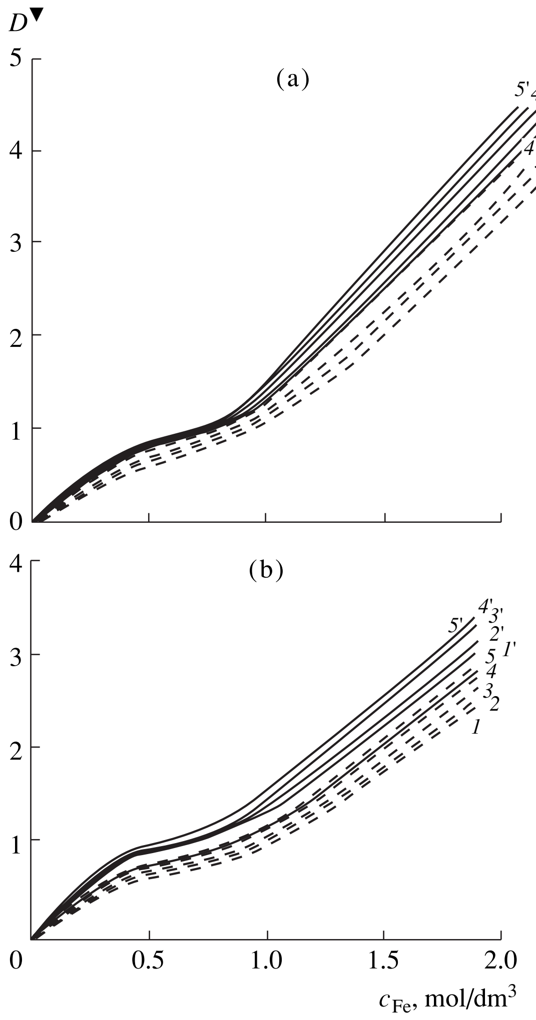


Fig. 2. $D^{\blacktriangledown}$ vs c_{Fe} for the Cu(II)–H_2L–Etl system at τ = (*1*, *1'*) 1, (*2*, *2'*) 2, (*3*, *3'*) 4, (*4*, *4'*) 6, and (*5*, *5'*) 10 min, c_{H_2L} = (– – –) 3.0×10^{-3}, (—) 1.2×10^{-2} mol/l; H_2L : Etl molar ratio (a) 0.50 and (b) 1.0. λ_{max} = 450 nm.

However, at c_{Fe} = 0.1–2.0, c_{H_2L} = 3.0×10^{-3}–2.0×10^{-1} mol dm^{-3}, τ = 2–10 min, and a dithiooxamide : ethanal molar ratio of 0.5 : 1.0, the gelatin layer turns greenish-brown due to the formation of compound **III**. This compound can be formed only when the $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrix is in contact with water–alkaline solutions simultaneously containing dithiooxamide and ethanal. If no ethanal is contained in the solution contacting with the matrix, the polymer layer of the matrix never turns this color, independent of the concentrations of dithiooxamide in the solution and copper(II) hexacyanoferrate(II) in the immobilized matrix. Thus, both dithiooxamide and ethanal participate in the complexation in the ternary system under study. The brown color of the polymer layer of the immobilized matrix can be due to one of the following reactions:

the Cu(II) $\longrightarrow$ Cu(I) redox process (it is well known that under certain conditions, the Cu(II) ion can oxidize organic compounds with C=O and C=S groups);

the formation of mixed-ligand Cu(II) coordination compounds with dithiooxamide and ethanal in the inner sphere;

transformations of dithiooxamide and ethanal in the inner sphere to yield Cu(II) complexes with a new ligand formed by these molecules.

After gelatin-immobilized matrices containing compound **III** were destroyed, greenish-brown products were isolated. Note that independent of the dithiooxamide : ethanal molar ratio in the solution in contact with the matrix, the products isolated were found to be the same chemical compound with the empirical formula $CuC_8S_4N_4OH_{12}$.

For $CuC_8S_4H_4OH_{12}$

anal. calcd.
(%): C, 25.85; H, 3.23; N, 15.06; Cu, 17.08; S, 34.48.
Found (%): C, 26.1; H, 3.3; N, 14.9; Cu, 17.3; S, 34.4.

Compound **III** is paramagnetic ($\mu_{eff} = 1.93\ \mu_B$) and exhibits an EPR signal with $g_{\parallel} = 2.20$ and $g_{\perp} = 2.04$ at 295–300 K. These data provide unambiguous evidence of the +2 oxidation state of copper, thus denying the possibility of the Cu(II) $\longrightarrow$ Cu(I) redox reaction.

No data on the complexation of Cu(II) with ethanal are available in the literature. The spectral parameters of the gelatin bulk did not change after the $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrices were treated with water–alkaline solutions of ethanal; therefore, one can conclude that Cu(II) does not form complexes with ethanal under the given conditions. This fact can be easily explained, provided Cu(II) is a mild Pearson acid (the orbital electronegativity of Cu(II) in aqueous solutions is equal to –0.55 [7]) while ethanal is a hard Pearson base. If the mixed-ligand complex of Cu(II) with dithiooxamide and ethanal is actually formed, one can expect that with an excess of ethanal the homoligand coordination compound of Cu(II) with ethanal will be formed in this system. Its color should be other than that of the homoligand Cu(II) chelate with dithiooxamide of 1 : 1 composition (according to [4], dark green) and of the mixed-ligand complex. In this case, the color should change first from dark green to greenish-brown and further to some other color. However, we did not observe such a change in the color of the immobilized matrix: a greenish-brown color also remained at dithiooxamide : ethanal molar ratios of noticeably less than 0.3. Moreover, special experiments were carried out which showed that none of the earlier known immobilized Cu(II) chelates with dithiooxamide [4] formed upon complexation in the $Cu[Fe(CN)_6]$ gelatin-immobilized matrix reacts with an aqueous alkaline solution of ethanal at any concentration or pH. These facts undoubtedly demonstrate that the specific greenish-brown color of the gelatin bulk that appeared upon complexation in the ternary system studied is not caused by the formation of mixed-ligand dithiooxamide–ethanal copper(II) complexes. Therefore, we should suggest that the third of the above-mentioned versions of complexation, i.e., the transformation of the initial organic compounds in the inner sphere to yield a new ligand, is realized with the participation of both dithiooxamide and ethanal. However, this "combined" ligand is not formed when aqueous solutions of dithiooxamide and ethanal are mixed: the electronic absorption spectrum of alkaline solutions of dithiooxamide (pH > 9.0) did not change after the addition of ethanal. The combined ligand can form only in the presence of a metal ion, in particular, Cu(II), which is a typical feature of template synthesis [8]. Thus, there are strong grounds to believe that the template synthesis takes place in the ternary Cu(II)–dithiooxamide–ethanal system upon complexation in the $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrices.

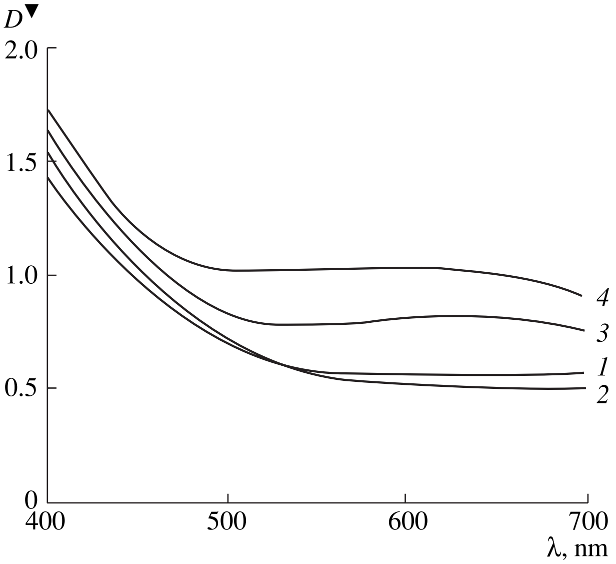
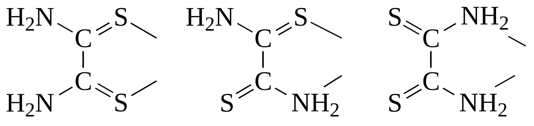


Fig. 3. Electronic absorption spectra of gelatin-immobilized matrices containing the coordination compounds formed in the Cu(II)–H_2L–Etl system at $c_{Fe} = 0.60$ mol/dm^3, $c_{H_2L} = 3.0 \times 10^{-3}$ mol/l, $\tau = 2$ min, H_2L : Etl molar ratio (*1*) 0.50, (*2*) 1.00, (*3*) 2.00 and (*4*) in the Cu(II)–H_2L system at $c_{Fe} = 0.60$ mol/dm^3, $c_{H_2L} = 1.0 \times 10^{-2}$ mol/l, and $\tau = 4$ min. The thickness of the polymer layer of the immobilized matrix was 20 μm.

Accounting for the foregoing and for the facts that dithiooxamide is ambidentate ligand and can form five-membered cycles with (S,S)-, (N,S)-, or (N,N)-donor centers

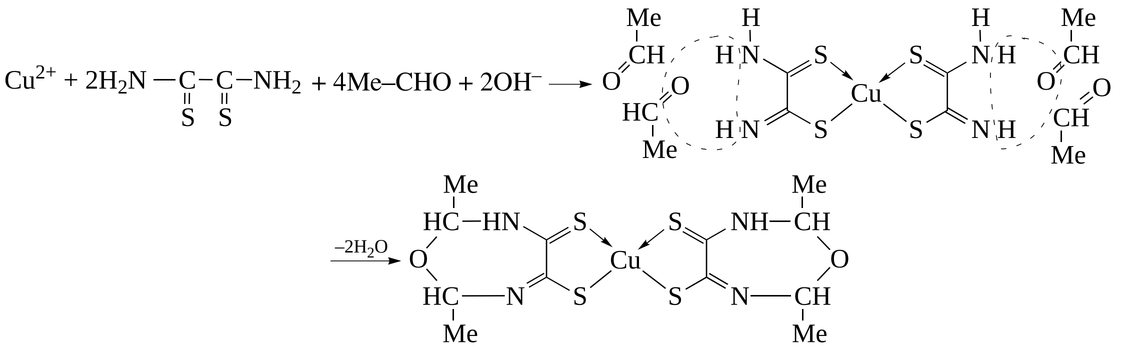


whereas ethanal can be, in principle, enolized to yield a reactive intermediate

$$H_3C–CH=O \longrightarrow H_2C=CH–OH,$$

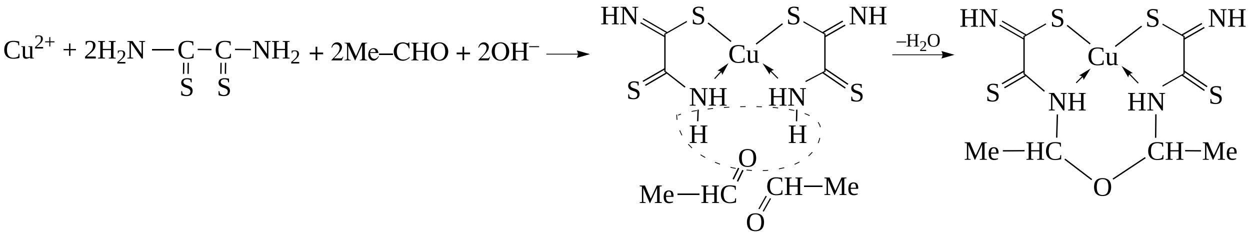
six possible versions of the template synthesis can be suggested to occur.

1. Cu(II) chelate with two S,S-donor ligands made up of a dithiooxamide molecule and two molecules of ethanal is formed with the detachment of two water molecules:



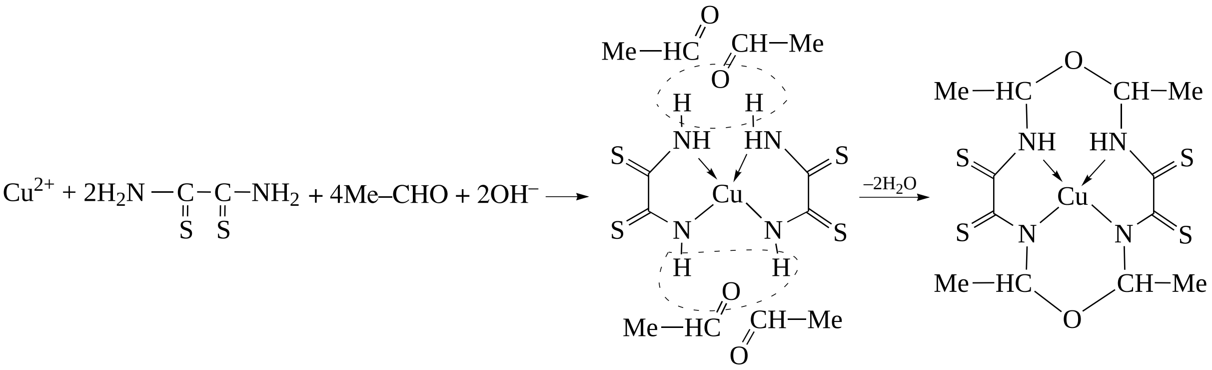
(1)

2. Cu(II) chelate with a tetradentate chelate N,N,S,S-donor ligand made up of two molecules of dithiooxamide and two molecules of ethanal is formed with the detachment of one water molecule:



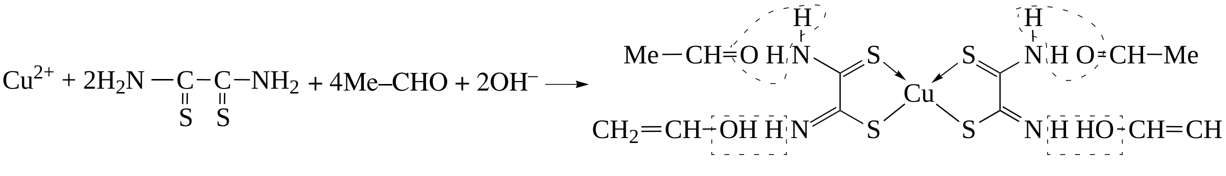
(2)

3. Cu(II) chelate with a tetradentate N,N,N,N-donor ligand made up of two molecules of dithiooxamide and four molecules of ethanal is formed with the detachment of two water molecules:

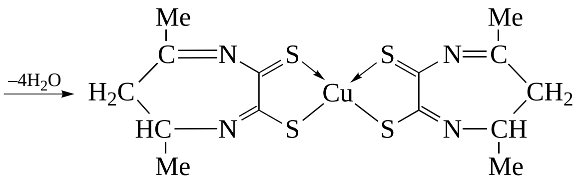


(3)

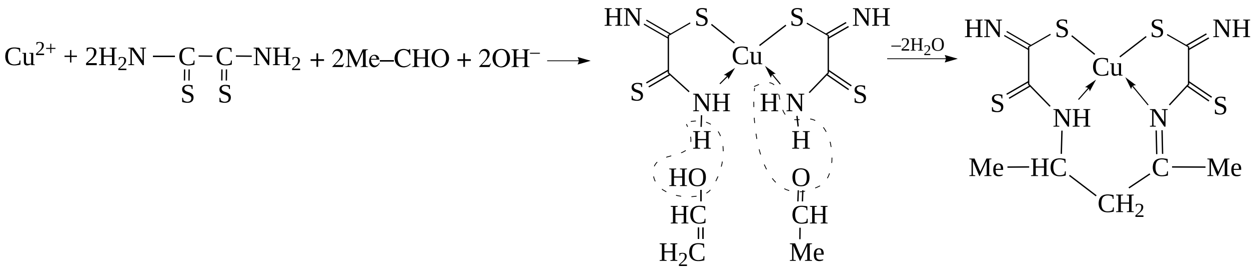
4. Cu(II) chelate with two S,S-donor ligands made up of a dithiooxamide molecule and two molecules of ethanal is formed with the detachment of four water molecules:



(4)

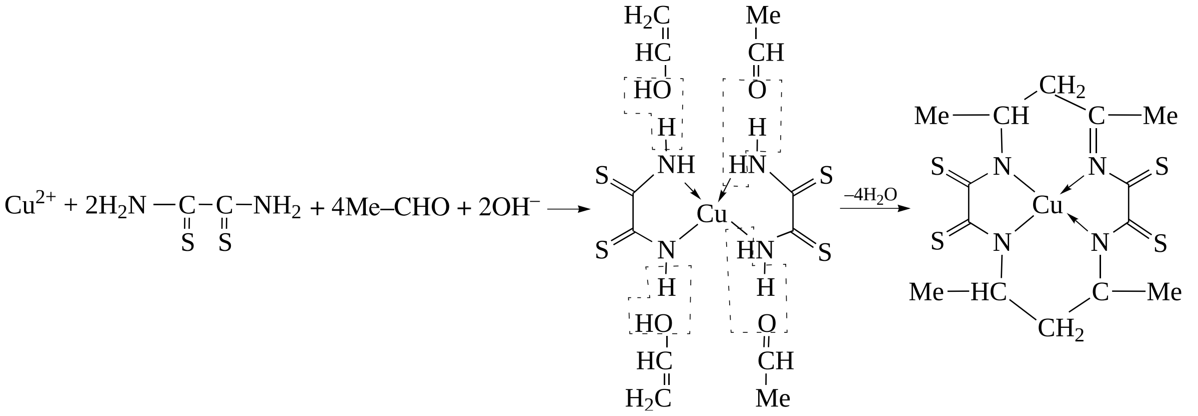


5. Cu(II) chelate with a tetradentate N,N,S,S-donor ligand made of two molecules of dithiooxamide and two molecules of ethanal is formed with the detachment of two water molecules:



(5)

6. Cu(II) chelate with a tetradentate N,N,N,N-donor ligand made of two molecules of dithiooxamide and four molecules of ethanal is formed with detachment of four water molecules:



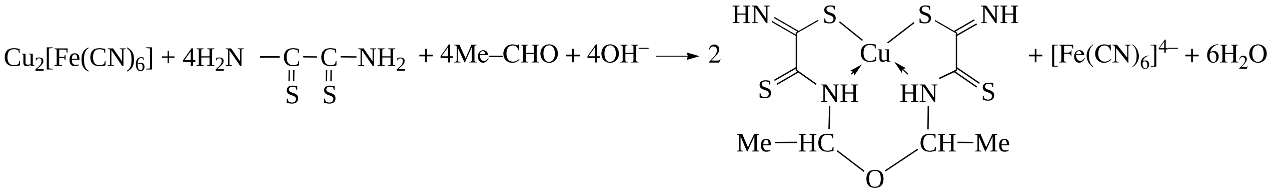
(6)

None of these versions can be *a priori* ruled out; therefore, it was necessary to verify how each of them agrees with experiment.

Mathematical analysis of the kinetic curves $D^{\blacktriangledown} = f(c_{\mathrm{Fe}}, c_{\mathrm{H_2L}}, \tau)$ at c_{Fe}, $c_{\mathrm{H_2L}}$, and τ corresponding to the formation of a greenish-brown compound **III** (see Figs. 1, 2) indicates that two molecules of dithiooxamide and two molecules of ethanal per Cu(II) ion are added (the amounts of this combined ligand and Cu(II) entering the reaction were calculated to be 0.9 and 1.1, respectively, which are close to the theoretical values of 1.0 and 1.0). These data fit versions (2) and (5). If version (2) is realized, the empirical formula of the complex should be $CuC_8S_4N_4OH_{12}$, while in the case of version (5), the empirical formula should be $CuC_9S_4N_4H_{12}$. Thus, only version (2) is consistent with the experimental data. The IR spectrum of complex **III** exhibits a broad ν(NH) band at ~3440 cm^{-1} that is characteristic of NH and NH_2 groups noncoordinated by the metal ion; therefore, at least some nitrogen atoms are not bound to Cu(II). Other characteristic bands in the IR spectrum (ν(C=S) at 645–650 cm^{-1}, which usually appear in the 570–705 cm^{-1} range; ν(C=N) at 1640–1645 cm^{-1}, which are usually observed in the 1625–1690 cm^{-1} range, ν(C–O–C) at 1115 cm^{-1} (usually observed at 1100–1200 cm^{-1}; and ν(CH_2) at 2865 and 2925 cm^{-1}, observed at 2845–2870 and 2915–2945 cm^{-1}, respectively) [9]) correspond to the composition and structure of the compound that is formed by scheme (2). Unfortunately, the bands observed in the IR spectrum of **III** in the frequency range <1000 cm^{-1} where, according to [9], the ν(Cu–N) and ν(Cu–S) bands should be exhibited cannot be unambiguously assigned to the stretching vibrations of the copper–nitrogen and copper–sulfur bonds.

The compound **III** isolated is stable on heating (according to DTA data, it is not destroyed even at 600°C) and is virtually insoluble in ethanol, acetone, chloroform, benzene, or carbon tetrachloride but is slightly soluble in dimethyl formamide, dimethyl sulfoxide, and hexamethyl phosphorus triamide. The electronic absorption spectra of **III** in dimethyl formamide and dimethyl sulfoxide solutions coincide with the spectra of the gelatin layers before its destroyed. This fact confirms the identity of the compound contained in the immobilized matrix with the product isolated.

Thus, template synthesis takes place upon complexation in a $Cu_2[Fe(CN)_6]$ gelatin-immobilized matrix in contact with the Cu(II)–dithooxamide–ethanal system and yields (2,8-dithio-3,7-diaza-4,6-dimethyl-5-oxanonanedithioamido-1,9)copper(II):



(7)

Unfortunately, we could not determine the crystal structure of the compound obtained, because very small crystals unsuitable for X-ray single-crystal analysis were formed in the course of its isolation from the immobilized matrices by the procedure used in this work and previously in [1, 2].

ACKNOWLEDGMENTS

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