# Low-Temperature Template Synthesis of [4,6,6-Trimethyl-2,6-dithioxo-3,7-diazanon-4-enebis(imidothioato)]copper(II) in Gelatin-Immobilized Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] Matrix Materials

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**Abstract**—Complexation in gelatin-immobilized copper(II) hexacyanoferrate(II) matrices on contact with alkaline (pH 10) aqueous solutions containing dithiooxamide and acetone was studied. Under these conditions, template synthesis occurs to give the chelate CuL [L is 4,6,6-trimethyl-2,6-dithioxo-3,7-diazanon-4-enebis-(imidothioato) ligand], with dithiooxamide and acetone acting as ligand synthons. The reaction pattern was suggested. Attempted reaction of dithiooxamide and acetone in solution in the absence of Cu(II) does not yield this ligand.

Previously [1-4] we have studied complexation reactions occurring on contact of gelatin-immobilized copper(II) hexacyanoferrate(II) matrix materials with aqueous solutions of dithiooxamide. The latter, in principle, can act as a so-called ligand synthon (ligson) in template synthesis [5, 6]. We believe [7] that immobilization of metal compounds can facilitate template synthesis under mild conditions, which was confirmed, in particular, in our previous papers [8, 9] by the examples of the reaction systems dithiooxamide + formaldehyde and dithiooxamide + glyoxal. In this work we examined the possibility of a similar synthesis in the system dithiooxamide + acetone.

When the gelatin-immobilized  $Cu_2[Fe(CN)_6]$  matrix material reacts with an alkaline solution containing dithiooxamide  $H_2NC(=S)C(=S)NH_2$  and acetone H<sub>3</sub>CC(=O)CH<sub>3</sub>, at concentrations of dithiooxamide  $C_{\rm L}^0 < 10^{-5}$  M, any concentrations of Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] in the matrix  $C_{\rm F}$ , dithiooxamide : acetone molar ratios of 0.5–2.0, and sufficiently long (t > 6 min) contact of the matrix with the solution, the initial red-brown color of the matrix changes to the grayish blue color, which is due to formation of compound **I**. The electronic spectrum of gelatin-immobilized matrices containing this substance exhibits a broad band with  $\lambda_{max}$  680–700 nm and coincides with the spectrum of gelatin-immobilized polymeric copper hydroxide  $[Cu(OH)_2]_n$  [1]. The breakdown of the matrix material allows isolation of a gray-blue substance which can be identified by chemical analysis as polymeric copper(II) hydroxide. Found, %: H 2.1; Cu 64.7;

O 33.2.  $(H_2CuO_2)_n$ . Calculated, %: H 2.04; Cu 65.31; O 33.61. Computer treatment of the kinetic curves  $D' = f(C_F, C_L^0, t)$  showed that in the examined concentration and time range  $(C_F, C_L^0, t)$  dithiooxamide or acetone molecules are not added, but two hydroxide anions are taken up per copper(II) ion. Thus, it is evident that in this system the complexation proper is preceded by transformation of copper(II) hexacyanoferrate(II) into polymeric copper(II) hydroxide, which is the initial form for subsequent transformations.

 $n\mathrm{Cu}_{2}[\mathrm{Fe}(\mathrm{CN})_{6}] + 4n\mathrm{OH}^{-} \rightarrow 2[\mathrm{Cu}(\mathrm{OH})_{2}]_{n} + n[\mathrm{Fe}(\mathrm{CN})_{6}]^{4-}.$ 

A similar phenomenon was already noted in [1–4, 10, 11] for the systems Cu(II)–dithiooxamide, Cu(II)–quinoxaline-2,3-dithiol, and Cu(II)–8-quino-linethiols.

At  $C_{\rm F} = 0.1-1.0$ ,  $C_{\rm L}^0 > 5.0 \times 10^{-2}$  mol dm<sup>-3</sup>, t = 2-10 min, and molar ratio dithiooxamide : acetone >2.0, compound **II** is formed, imparting a dark green color to the gelatin layer. The spectral characteristics of this layer coincide with those of the complex [Cu(HL)<sub>2</sub>]<sub>n</sub> (H<sub>2</sub>L is dithiooxamide) described in [1-4]. On breakdown of the gelatin matrix containing **II**, a black-green compound is isolated with the empirical formula C<sub>4</sub>H<sub>6</sub>CuN<sub>4</sub>S<sub>4</sub>, consistent with the composition [Cu(HL)<sub>2</sub>]<sub>n</sub>. Found, %: C 15.8; H 2.1; Cu 21.0; N 18.8; S 42.2. C<sub>4</sub>H<sub>6</sub>CuN<sub>4</sub>S<sub>4</sub>. Calculated, %: C 15.89; H 1.98; Cu 21.19; N 18.55; S 42.39. However, at  $C_{\rm F} = 0.1-2.0$ ,  $C_{\rm L}^0 = 3.0 \times 10^{-3}-2.0 \times 10^{-1}$  mol dm<sup>-3</sup>, t = 2-10 min, and molar ratio dithiooxamide : ace-



**Fig. 1.** Curves  $D' = (C_F, C_L^0, t)$  in the system Cu(II)-dithiooxamide-acetone in the cordinate section  $[C_F = \text{const, varied } C_L^0, \text{ variable } t]$  at the dithiooxamide : acetone ratio of (a) 0.50 and (b) 1.00. Dithiooxamide concentration  $C_L^0$ , M:  $(I, I') 3.0 \times 10^{-3}$ ,  $(2, 2') 6.5 \times 10^{-3}$ , and  $(3, 3') 1.2 \times 10^{-2}$ ;  $C_F$ , mol dm<sup>-3</sup>: (*dashed line*) 0.70 and (*solid line*) 1.00. The optical densities D' were measured with a light filter with  $\lambda_{\text{max}}$  450 nm.



**Fig. 2.** Curves  $D = (C_{\rm F}, C_{\rm L}^0, t)$  in the system Cu(II)-dithiooxamide-acetone in the coordinate section  $[C_{\rm L}^0 = \text{const}, \text{ variable } t, \text{ variable } C_{\rm F}]$  at the dithiooxamide : acetone ratio of (a) 0.50 and (b) 1.00.  $C_{\rm L}^0$ , M: (I)  $3 \times 10^{-3}$ , (II)  $6.5 \times 10^{-3}$ , and (III)  $1.2 \times 10^{-3}$ ; t, min: (I) 1, (2) 2, (3) 4, (4) 6, and (5) 10. The optical densities D' were measured with a light filter with  $\lambda_{\rm max}$  450 nm.

tone = 0.5-1.0, compound **III** is formed, imparting to the gelatin matrix a greenish brown color (Figs. 1–3). It is significant that this compound is formed only on contact of the gelatin-immobilized copper(II) hexacyanoferrate matrix with aqueous alkaline solutions containing dithiooxamide and acetone simultaneously. It should be particularly emphasized in this connection that in the absence of acetone no compounds of such a color are formed in the system at any concentrations of dithiooxamide in solution and copper(II) hexacyanoferrate(II) in the gelatin matrix (Fig. 3). This means that dithiooxamide and acetone simultaneously participate in the complexation. In this connection, the brown coloration of the polymeric matrix layer may be due either to the reduction  $Cu(II) \rightarrow$ Cu(I) [it is well known that under appropriate conditions Cu(II) oxidizes organic compounds containing carbonyl and thiocarbamoyl groups], to formation of heteroligand coordination compounds of copper(II) with dithiooxamide and acetone in the inner sphere, or, finally, to inner-sphere transformations of dithiooxamide and acetone yielding Cu(II) complexes with certain new ligands "constructed" from the above molecules. The correct alternative can be chosen by comparing the experimental data with the theoretical expectations.

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**Fig. 3.** Electronic absorption spectra of gelatin-immobilized coordination compounds formed (*1–3*) in the system Cu(II)–dithiooxamide–acetone at  $C_{\rm F} = 0.60 \text{ mol dm}^{-3}$ ,  $C_{\rm L}^0 = 3.0 \times 10^{-3}$  M, t = 2 min, and ratio of the initial ligsons of (*1*) 0.50, (*2*) 1.00, and (*3*) 2.00, and (*4*) in the system Cu(II)–dithiooxamide at  $C_{\rm F} = 0.60 \text{ mol dm}^{-3}$ ,  $C_{\rm L}^0 = 1.0 \times 10^{-2}$  M, and t = 4 min. Thickness of the matrix polymer layer 20  $\mu$ m.

When the gelatin matrices containing III are broken down, brown substances with the empirical formula  $C_{10}H_{14}CuN_4S_4$  are isolated. These compounds are paramagnetic ( $\mu_{eff} = 1.94 - 1.96 \mu_B$ ) and at 295–300 K give an ESR signal with  $g_{\parallel} = 2.24 - 2.26$  and  $g_{\perp} =$ 2.07–2.09, which unambiguously indicates the copper oxidation state +2 and rules out the redox process  $Cu(II) \rightarrow Cu(I)$ . All these substances contain no oxygen and have the same empirical formula (see above), irrespective of the dithiooxamide : acetone molar ratio in the contacting solution (varied in the range 0.5-1.0). Found, %: C 31.8; H 3.6; Cu 16.4; N 15.0; S 33.0.  $C_{10}H_{14}CuN_4S_4$ . Calculated, %: C 31.45; H 3.67; Cu 16.63; N 14.67; S 33.58. The absence of oxygen rules out formation of heteroligand complexes of Cu(II) incorporating acetone.

There are no published data on complexation of Cu(II) with acetone; the spectral characteristics of the gelatin-immobilized  $Cu_2[Fe(CN)_6]$  matrix do not change on contact with alkaline solutions of acetone, which indicates that no acetone complexes are formed under these conditions. This fact is quite natural, as acetone, according to the Pearson's concept, is a hard base, whereas Cu(II) is a soft acid {the orbital electronegativity of Cu(II) in aqueous solutions is -0.55 [12]}. In special experiments we detected no reaction of aqueous-alkaline acetone solution with any of the known [1–4] immobilized Cu(II) chelates with dithiooxamide formed by complexation in the gelatin-immobilized  $Cu_2[Fe(CN)_6]$  matrix, irrespective of pH and acetone concentration in solution. These facts

suggest that in our system a certain new ligand is formed, involving both dithiooxamide and acetone. It is significant that this "combined" ligand is not formed on simple mixing of aqueous solutions of dithiooxamide and acetone containing no copper: The absorption spectra of aqueous-alkaline (pH > 9.0) solutions of dithiooxamide do not change on adding acetone. Hence, the new ligand can form only in the presence of a metal ion, in particular, Cu(II), i.e., we apparently deal with a template synthesis in the system Cu(II)–dithiooxamide–acetone in the gelatin-immobilized Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] matrix.

Dithiooxamide is an ambidentate ligand; it can, in principle, form five-membered rings with (S,S), (N,S), or (N,N) coordination:



Based on the whole set of the experimental data and on theoretical considerations, we can suggest the following alternatives of the template synthesis in the ternary system under consideration:

(a) Formation of a Cu(II) coordination compound with two (S,S)-donor chelating ligands, each being formed by condensation of one dithiooxamide molecule with two acetone molecules [scheme (1)]:



(b) Formation of a copper(II) coordination compound with the (N,N,S,S)-donor chelating ligand constructed from two dithiooxamide and two acetone molecules [scheme (2)]:



(c) Formation of a Cu(II) complex with the (N,N,N,N)-donor ligand constructed from two dithio-oxamide and four acetone molecules [scheme (3)]:



It is well known that acetone is characterized by the keto-enol tautomerism [scheme (4)]:



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Although the content of the enol form is insignificant (the molar ratio of the enol and keto forms in water at  $25^{\circ}$ C is  $1:10^{6}$ ) [13], it can participate in reactions as intermediate species, and three theoretically possible reaction pathways involving the enol form should be considered.

(d) Formation of a Cu(II) complex with two (S,S)donor chelating ligands. This case is similar to that described by scheme (1) in that each ligand is constructred from one dithiooxamide molecule and two acetone molecules, but intramolecular dehydration results in removal of four, and not two, water molecules [scheme (5)]:



(e) Formation of a Cu(II) complex with the (N,N,S,S)-donor ligand formed by scheme (6), which resembles scheme (2) but involves removal of a double amount of water.



(f) Formation of a Cu(II) complex with the (N,N,N,N)-donor ligand formed from two dithiooxamide and four acetone molecules by scheme (7), which resembles scheme (3) but involves removal of four water molecules.



The product formed by any of schemes (1)–(3)should contain oxygen, which is inconsistent with the actual empirical formula, C4H6CuN4S4. Hence, if in our ternary system the template synthesis takes place, it can occur only by schemes (5)-(7). The isolated product is practically insoluble in such organic solvents as ethanol, acetone, chloroform, benzene, and tetrachloromethane and slightly soluble in dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide. The electronic spectra of dimethylformamide and dimethyl sulfoxide solutions of this compound practically coincide with the spectra of the gelatin layers from which the compound was isolated. The DTA data show that the compound is very stable to heating and does not undergo thermolysis even at 600°C. The IR spectrum of the complex contains a broad v(NH) band at  $3400-3500 \text{ cm}^{-1}$ , characteristic of noncoordinarted NH or NH<sub>2</sub> groups; hence, at least a part of nitrogen atoms remains noncoordinated. The spectra contain also the bands v(C=S) at 680 cm<sup>-1</sup> (commonly observed in the range  $570-705 \text{ cm}^{-1}$ ) and v(C=N) at 1645 cm<sup>-1</sup> (commonly observed at 1625– 1690  $\text{cm}^{-1}$  [14]). Unfortunately, in the wave number

range  $<1000 \text{ cm}^{-1}$  in which, according to [14], the v(Cu-N) and v(Cu-S) bands should be expected, the observed bands cannot be assigned unambiguously. The spectra contain bands at 2850 and 2930 cm<sup>-1</sup>, which, according to [14], can be assigned to  $v(CH_2)$ . All these facts are consistent with the structure of the product formed by scheme (6). The results of the mathematical analysis of the kinetic curves D' = $f(C_{\rm F}, C_{\rm L}^0, t)$ , performed according to [15] for the range  $(C_{\rm F}, C_{\rm L}^0, t)$  in which the brown complex is formed, show that the template synthesis involves addition of two dithiooxamide and two acetone molecules per Cu(II) ion. The stoichiometric ratio of the ligand and Cu(II) in the elementary reaction event, calculated from the experimental data, is 1.0: 1.2, which is close to the theoretical ratio of 1.0: 1.0. It can be readily seen that only scheme (6) is consistent with the whole set of the experimental data, including the empirical formula of the product,  $C_4H_6CuN_4S_4$  (III).

Thus, we can conclude that in the system Cu(II)– dithiooxamide–acetone under specific conditions of complexation in the gelatin-immobilized  $Cu_2[Fe(CN)_6]$ matrix a template synthesis occurs yielding [4,6,6-trimethyl-2,8-dithioxo-3,7-diazanon-4-enebis(imidothioato)]copper(II) according to Eq. (8):



It is interesting that the structure of the template synthesis product formed in the system Cu(II)–dithiooxamide–acetone differs significantly from that for coordination compounds detected previously in the systems M(II)–dithiooxamide–formaldehyde (M = Co, Ni, Cu) [8, 16, 17]. However, a similar difference was observed previously [5, 6] between the systems M(II)– 1,2-ethylenediamine–formaldehyde and M(II)–1,2ethylenediamine–acetone (M = Ni, Cu).

#### EXPERIMENTAL

The optical densities of gelatin-immobilized metal chelate matrices were measured in the transmission mode with a Macbeth TD-504 photometer (working range of optical density 0.1–5.0, accuracy  $\pm 2$  rel.%). The electronic absorption spectra were taken with a Specord UV–Vis spectrophotometer in the range 400–800 nm with an accuracy of  $\pm 2$  rel.%. The IR spectra were taken with a UR-20 spectrometer. The pH values were measured on a pH-340 pH meter with an accuracy of  $\pm 0.05$ . The ESR spectra were recorded with a Bruker ESR-200D spectrometer at 298 K.

Gelatin-immobilized Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] matrix materials were prepared as described in [1-4]. The materials were treated with aqueous-alkaline solutions containing dithiooxamide and acetone in a ratio of (0.5-2.0): 1. The dithiooxamide concentration in solution was  $1.0 \times 10^{-3}$ - $5.0 \times 10^{-2}$  M, at fixed pH  $12.0 \pm 0.1$ and temperature ( $20.0\pm0.1^{\circ}$ C). The contact time of the gelatin-immobilized  $Ce_2[Fe(CN)_6]$  matrix materials with the ligson solutions was 1-10 min. After complexation completion, the gelatin matrix was washed in running water for 15 min and dried for 2-3 h at room temperature. The complexation kinetics were described by the dependences  $D' = f(C_F, C_L^0, t)$ , where D' is the optical density of the gelatin-immobilized metal chelate matrix material corresponding to the intitial concentration of  $Cu_2[Fe(CN)_6]$  in the matrix  $C_{\rm F}$ , mol dm<sup>-3</sup>, dithiooxamide concentration in solution  $C_{\rm L}^0$ , M, and process time t, min. Computer treatment of these dependences was performed by the PTKDCGIM program based on the approach described in [15]. To determine the composition of coordination compounds formed in the gelatin matrices, the products were isolated by breaking down the matrix with solutions of proteolytic enzymes [18]. The compounds were washed, dried, and analyzed by common procedures.

Special experiments showed that the complexation pathway is independent of the kind of gelatin. This fact suggests that, similar to the other known systems metal ion–(N, O, S)-donor chelating ligand [7], gelatin does not participate in complexation as ligand. All chemicals used for preparing gelatin-immobilized Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] matrices and performing complexation were of analytically pure or chemically pure grade and were used without additional purification.

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