Copper(II)- Heterocyclic Compounds with 4,5-Dimethyl-2,3,6,7-tetraazaoctadien-3,5-dithiohydrazide-1,8 and 3,10-Dithio-6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradekatetraen-1,5,7,12 Obtained in Gelatin- Immobilized Matrix as a Result of Template Synthesis

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♦ *Abstract*

Soft template synthesis of macrocyclic coordination compounds with 4,5-dimethyl-2,3,6,7-tetraaza-octadien-3,5-dithiohydrazide-1,8 and 3,10-dithio-6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclo-tetradekatetraen-1,5,7,12 in the triple Cu(II)-thiocarbohydrazide- 2,3- butanedione system in the copper(II)hexacyanoferrate(II) gelatin-immobilized matrix has been carried out. Also, it has been established that similar process in the nickel(II)hexacyanoferrate(II) matrices does not occur under such conditions.

♦ *Introduction*

It is known that the processes of template synthesis which afford the possibility of constructing chelate complexes with macrocyclic ligands from simpler fragments - ligand synthons, occur in solutions and solid phase mostly under rather drastic conditions. It could be believed nevertheless that the specific conditions formed upon complexing in gelatin-immobilized matrices (GIM), for example in metalhexacyanoferrate(II) ones [1-4], would enable at least certain template processes to occur under soft conditions, primarily at room temperature. Data of works published before [5-8] evidences that, indeed, such «soft» template synthesis may be quite realized in specific conditions indicated. We would like to report in this communication that we were able to carry out such a synthesis involving $Cu_2[Fe(CN)_6]$-gelatin-immobilized matrix and such ligand synthons as thiocarbohydrazide $H_2N\text{-}HN\text{-}C(=S)\text{-}NH\text{-}NH_2$ and 2,3-butanedione $H_3C\text{-}C(=O)\text{-}C(=O)\text{-}CH_3$ and to obtain three macrocyclic coordination compounds of Cu(II) with a two novel before unknown tetradentate ligands- 4,5-dimethyl-2,3,6,7-tetraazaoctadien-3,5-dithiohydrazide-1,8 and 3,10-dithio-6,7,13,14-tetramethyl-1,2,4,5,8,9,11, 12-octaazacyclotetradekatetraen -1,5,7,12.

♦ *Experimental*

$M_2[Fe(CN)_6]$-GIM (M= Ni, Cu) were synthesized as described before in [1-3].

Synthesis of $CuC_6S_2N_8OH_{14}$, $CuC_6S_2N_8O_2H_{16}$ and $CuC_{10}S_2N_8H_{14}$. Such as synthesis occurs on contact of $Cu_2[Fe(CN)_6]$- GIM with alkaline solutions (pH=11-12) containing thiocarbohydrazide and 2,3-butanedione. The concentration of copper(II) hexacyanoferrate(II) in the GIM was 0.1-2.0 mol dm^{-3}, the concentration of thiocarbohydrazide and 2,3-butanedione in the solution was $(1.0\cdot10^{-2} - 1.0\cdot10^{-1})$ $mol\,l^{-1}$. The duration of the process was 10-12 min at 18-20°C. The isolation of substances immobilized in the metalchelate gelatin matrix obtained was made according to technique described in [4]. Finally, the substances isolated from GIM was washed with distilled water, ethanol and dried at the room temperature.

The transmitted light absorbance of the GIMs ($D^{\blacktriangledown}$) were measured with a Macbeth TD504 photometer (Kodak Co., USA) in the 0.1-5.0 absorbance units range with an accuracy of $\pm 2\%$ (rel.). Mass spectra of substances isolated from GIMs were measured with using Dynamo (Fimigan) and 4-nitroanyline matrix at frequence 500MHz and laser power 55.25 units.

Electron absorption spectra of the GIMs were recorded using Specord UV-VIS (Karl Zeiss, Germany) and PU-8710 (Philips, The Netherlands) spectrophotometers in the 400-800 nm range. In order to record IR spectra, a Specord-80 spectrometer (Karl Zeiss, Germany) was employed.

◆ *Results & Discussion*

MALDI TOF mass-spectra of substances isolated from gelatin-immobilized matrices since the end of complexing process showed the availability of three peaks of molecular ions having molecular mass $M_I = 343$ c.u., $M_{II} = 360$ c.u. and $M_{III} = 374$ c.u. Computer-chemical analysis of possible products of complexing process in the triple system Cu(II)- thiocarbohydrazide- 2,3-butanedione under examination evidenced that the molecular masses indicated might to correspond *only* to (4,5-dimethyl-2,3,6,7- tetra- azaoctadien-3,5-dithiohydrazide-1,8)hydroxocopper(II) $CuC_6S_2N_8OH_{14}$ (I), (4,5-dimethyl-2,3,6,7-tetraazaoctadien-3,5-dithiohydrazide-1,8)dihydroxocopper(II) $CuC_6S_2N_8O_2H_{16}$ (II) and (3,10-dithio-6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradekatetraen-1,5,7,12) copper(II) $CuC_{10}S_2N_8H_{14}$ (III) (calculated values of molecular mass are 341.9, 359.9 and 373.9 c.u., respectively). No other compounds which might be theoretically formed at the complexing process in the above system, cannot have molecular masses indicated. It is significant that an intensity of peak corresponding M_I and M_{II} *decreases* with decrease thiocarbohydrazide: 2,3-butanedione molar ratio whereas an intensity of peak corresponding M_{III} *increases*; besides, a full disappearance of even only one of these peaks in the mass-spectrum is not observed at any thiocarbohydrazide: 2,3-butanedione ratio. In this connection, no doubt that in the system considered, a formation of *three various* coordination compounds occurs. This conclusion is in full agreement with the data of the mathematical analysis of $D^{\vee}=f(C_F,C_I{}^0,t)$ kinetic curves of complexing process according to known procedure [9] ($D^{\vee}$ is the optical density of the metal-chelate GIM corresponding to concentration of copper(II)hexacyanoferrate(II) in the matrix (C_F), thiocarbohydrazide in solution ($C_L{}^0$) and the duration of the complexing process t) for the various thiocarbohydrazide: 2,3-butanedione molar ratio in the range 0.1-2.0. According to this data, at $C_L{}^0= (2.5\,10^{-2} - 7.5\,10^{-2})$ mol·l^{1} in the range 0.1-0.4, an addition of two thiocarbohydrazide molecules and two 2,3-butanedione ones per metal (II) ion occurs whereas in the range 1.0-2.0, an addition of two thiocarbohydrazide molecules and only one 2,3-butanedione ones per metal(II) ion. The resulting compounds colour the polymeric masses of the GIM red-brown. The chemical analysis data: for compound (I) found (%): Cu, 18.3; C, 21.4; S, 18.5; N, 32.6; H, 4.0, $CuC_6S_2N_8OH_{14}$, calc. (%): Cu, 18.58; C, 21.08; S, 18.75; N, 32.78; H, 4.13; for compound (II) found (%): Cu, 17.5; C, 20.0; S, 18.0; N, 30.9; H, 4.4, $CuC_6S_2N_8O_2H_{16}$, calc. (%): Cu, 17.65; C, 20.02; S, 17.81; N, 31.14; H, 4.48; for compound (III) found (%): Cu, 17.1; C, 32.3; S, 17.4; N, 28.9; H, 3.9, $CuC_{10}S_2N_8H_{14}$, calc. (%): Cu, 16.99; C, 32.12; S, 17.15; N, 29.17; H, 3.77. At the same time, it is significant that at $C_L{}^0 < 10^{-5}$ mol·l^{-1}, at the such a contact, an addition of thiocarbohydrazide or 2,3-butanedione to Cu(II) does not occur and in the GIM forms only polymeric copper(II)hydroxide $[Cu(OH)_2]_n$ colours gelatin mass grey-blue. The circumstance noted is evidence that $[Cu(OH)_2]_n$ formation precedes complexing process. It should be noted especially in this connection that at in absence of 2,3-butanedione, the polymer mass of the GIM since the end of complexing reaction have grey-green colour corresponding colour of the known Cu(H) chelate with thiocarbohydrazide. Besides, in the mass spectrum of substance isolated from metalchelate GIM formed in the absence of 2,3-butanedione, nobody of M_I, M_{II} and M_{III} peaks is observed. At the same time, in absence of thicarbohydrazide, only an «alkaline destruction» of $Cu_2[Fe(CN)_6]$ with formation of polymeric copper(II) hydroxide well known from literature [1,3] occurs. No doubt that both thiocarbohydrazide and 2,3-butanedione simultaneously participate in the complexing process that occurs under these specific conditions. Finally, the UV-VIS absorption spectra in the

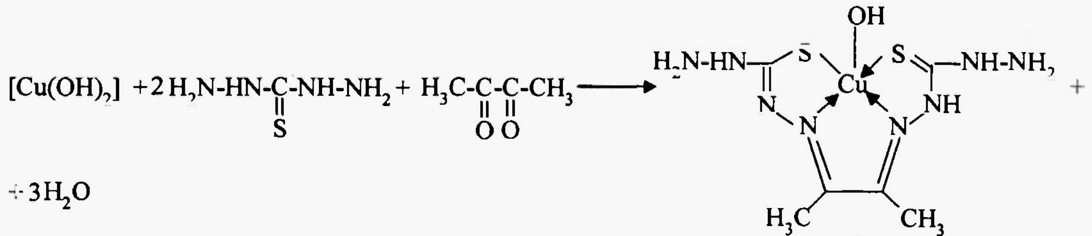
range of 400-700 nm of aqueous solutions of thiocarbohydrazide of any concentrations at pH>10 did not change even on addition of significant amounts of 2,3-butanedione for at least 2 days, and no indications of a chemical process between thiocarbohydrazide and 2,3-butanedione was observed. Hence, the reaction between the reagents indicated above does not occur in the absence of a copper(II) ion at all. A similar phenomenon is possible only in template synthesis [10-15]. Besides, thiocarbohydrazide and 2,3-butanedione are ligand synthons.

Decomposition of the polymeric binder of GIM by enzymes according to the known procedure [4] allowed us to isolate red-brown substances which is almost insoluble in water, ethanol, acetone, chloroform, benzene and tetrachloromethane, and poorly soluble in dimethylformamide and dimethylsulfoxide. The UV-VIS spectra of dimethylformamide and dimethylsulfoxide solutions of these substances under examination are almost identical to those of their source GIM indicating that the immobilized compounds are the same as that isolated from these immobilized matrices. The DTA data indicate that substances isolated from metal-chelate GIM is heat-resistant and at 400°C do not undergo pyrolysis yet.

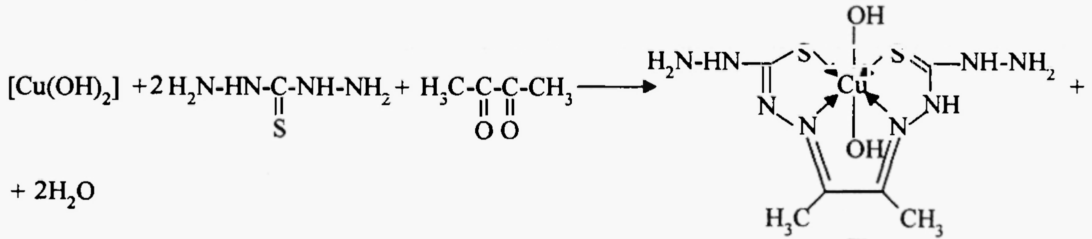
There are only three characteristic bands in the IR spectra of compounds (I) and (II) which may be identified: 720-725 cm^{-1} (ν(C–S)); 755-760 cm^{-1} (ν(C=S)) and 1640-1650 cm^{-1} (ν(C=N)); at the same time, there is a wide band in the 3200-3300 cm^{-1} in spectrum of each of these compounds which may be related to a superposition of intense bands corresponding to ν(OH) and $\nu(NH_2)$. The availability of these bands is in agreement with the structures proposed for these coordination compounds. In the IR spectrum of compound (III), however, there are ν(C=S) and ν(C=N) bands (at 760 and 1645 cm^{-1}, respectively) whereas first of these bands is not observed. In this connection, it is interesting to note that a bands corresponding to $\nu(NH_2)$ and observed in the IR spectrum of thiocarbohydrazide at 3200 and 3270 cm^{-1}, in the IR spectrum of compound (III) is absent; this circumstance is just one more evidence that it does not contain NH_2 groups. NMR ^{13}C spectra of compounds (I) and (II) show four signals, NMR ^{13}C spectrum of compound (III), only two ones.

By taking into consideration the all foregoing, the following schemes of template synthesis proceeding at an interaction between Cu(II), thiocarbohydrazide and 2,3- butanedione in the $Cu_2[Fe(CN)_6]$- GIM leading to formation of copper-containing heterocyclic compounds I, II and III, may be written:

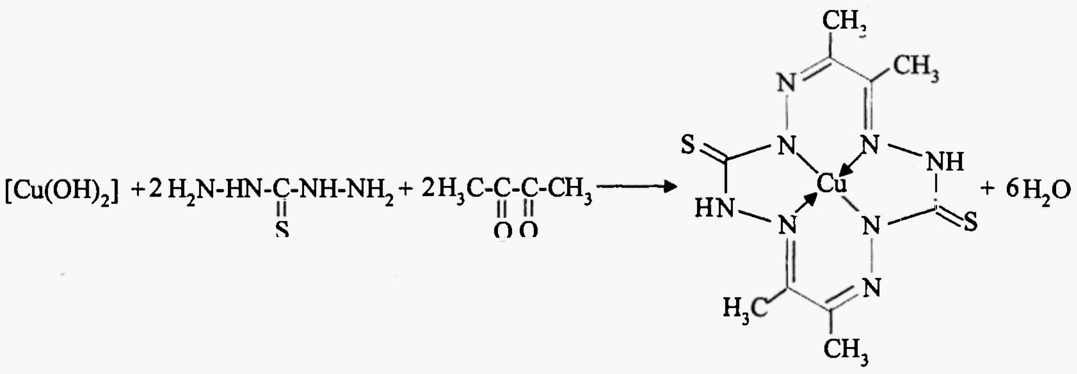
$$nCu_2[Fe(CN)_6] + 4nOH^- \longrightarrow 2\,[Cu(OH)_2]_n + n[Fe(CN)_6]^{4-}$$



I



II



III

It should be specially mentioned that processes of template synthesis between Cu(II), thiocarbohydrazide and 2,3-butanedione at room temperature occurs *only in GIM;* nobody of them does not occur at the contact $Cu_2[Fe(CN)_6]$ with the reagents indicated in solution or in the solid phase at such temperaturic conditions. At the same time, at the contact of $Ni_2[Fe(CN)_6]$-GIM with solution containing thiocarbohedrazide and 2,3- butanedione, any changes of D^{*} values even at long time of contact are not observed; this circumstance evidences that complexing process in the Ni(II)- thiocarbohydrazide- 2,3-butanedione system in the $Ni_2[Fe(CN)_6]$-GIM similar to complexing process in the Cu(II)- thiocarbohydrazide- 2,3-butanedione system in the $Cu_2[Fe(CN)_6]$-GIM, does not take place at all. These facts indicate the specific role of gelatin-immobilized matrix as organizing system in template reactions studied.

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