# Mild template synthesis in the $Co^{II}$—dithiooxamide—glyoxal system in cobalt(II) hexacyanoferrate(II) gelatin-immobilized matrices

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Complexation processes in a cobalt(II) hexacyanoferrate(II) gelatin-immobilized matrix under the action of aqueous solutions containing dithiooxamide $H_2N-C(S)-C(S)-NH_2$ and glyoxal HOC—CHO at pH > 10 were studied. Under these conditions, mild template synthesis occurs to form a $Co^{III}$ chelate with the (N,N,S,S)-ligand, *viz.*, 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8, with a metal to ligand ratio of 1 : 1, where dithiooxamide and glyoxal act as ligand synthons. The reaction mechanism is discussed.

**Key words:** gelatin-immobilized matrix; hexacyanoferrate(II); cobalt complexes; chelate; complexation; template synthesis.

Previously,[1—3] complexation in the $Co^{III}$—dithiooxamide system upon interaction of cobalt(II) hexacyanoferrate(II) in a gelatin-immobilized matrix (GIM) with aqueous solutions of dithiooxamide has been studied. The latter can act as a ligand synthon (ligson) in the course of template synthesis.[4,5] We have suggested[6] that immobilization of metal compounds may favor the template synthesis under mild conditions. In the present work, we studied the possibility of template synthesis in this system with the use of an additional ligson, *viz.*, glyoxal.

## Experimental

The synthesis of $Co_2[Fe(CN)_6]$-GIM was carried out according to a known procedure.[7] The resulting matrix was treated with aqueous-alkaline solutions of dithiooxamide and glyoxal at pH 12.0±0.1; the concentrations of dithiooxamide were $3.0 \cdot 10^{-3}$—$3.0 \cdot 10^{-2}$ mol $L^{-1}$; the molar ratios of the reagents were 0.5—2.0. The time of interaction of the cobalt(II) hexacyanoferrate(II) gelatin-immobilized matrix with these solutions was varied from 1 to 10 min at 20.0±0.1 °C. After completion of the process, the gelatin bulks were washed with running water for 15 min and dried at ambient temperature for 2—3 h. The kinetics of complexation was described by the relationships $D' = f(C_f, C_l^0, t)$, where $D'$ is the optical density of metal-chelate GIM corresponding to the initial concentration of $Co_2[Fe(CN)_6]$ in the matrix ($C_f$/mol $L^{-1}$), the concentration of dithiooxamide in the solution ($C_l^0$/mol $L^{-1}$), and the duration of the process ($t$/min). The stoichiometric coefficients in the equations for elementary stages of complexation were determined using the coordinate sections [$C_f$ = const, variables $C_l^0$, and arguments $t$] and [$C_l^0$ = const, variables $t$, and arguments $C_f$], which were analyzed according to a procedure reported previously.[8,9] Examples of these dependences are shown in Figs. 1—3. For the purpose of determining the bulk chemical compositions of the coordination compounds formed in GIM, these compounds were isolated from the corresponding matrices using solutions of proteolytic enzymes as described previously.[10] After washing and drying, the compounds were characterized by elemental analysis according to a standard procedure.

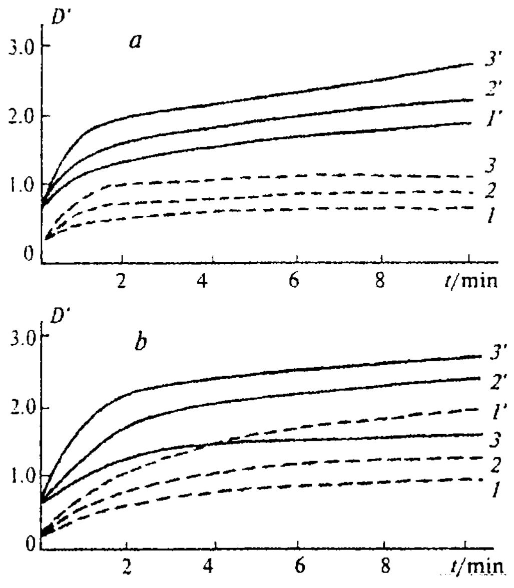

**Fig. 1.** Curves $D' = f(C_f, C_l^0, t)$ for the $Co^{II}$—dithiooxamide—glyoxal system in the coordination section ($C_f$ = const, variables $C_l^0$, and arguments $t$); the dithiooxamide : glyoxal ratio is 0.50 (*a*) and 1.00 (*b*). The concentrations of dithiooxamide $C_l^0$/mol $L^{-1}$ are $3.0 \cdot 10^{-3}$ (curves *1* and *1'*), $6.0 \cdot 10^{-3}$ (*2* and *2'*), and $1.2 \cdot 10^{-2}$ (*3* and *3'*); $C_f$ = 0.19 mol $L^{-1}$ (dashed line) and 0.38 mol $L^{-1}$ (solid line). The optical densities $D'$ were measured with the use of a light filter with $\lambda_{max}$ = 450 nm.

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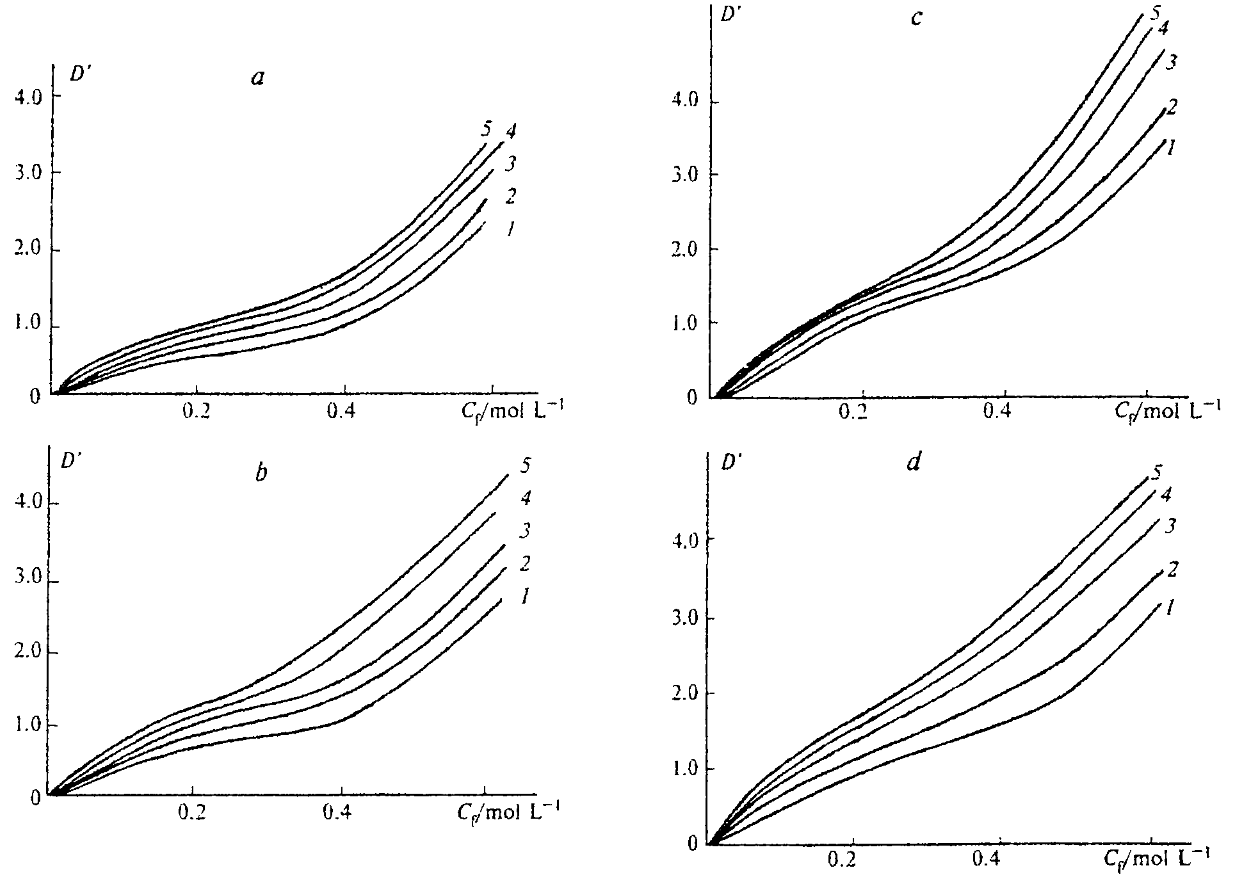


**Fig. 2.** Curves $D' = f(C_f, C_l^0, t)$ for the Co$^{II}$—dithiooxamide—glyoxal system in the coordination section ($C_l^0$ = const, variables *t*, and arguments $C_f$); the dithiooxamide : glyoxal ratio is 0.50 (*a* and *c*) and 1.00 (*b* and *d*). $C_l^0 = 3.0 \cdot 10^{-3}$ mol L$^{-1}$ (*a* and *b*) and $C_l^0 = 6.0 \cdot 10^{-3}$ mol L$^{-1}$ (*c* and *d*), *t*/min = 1 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), and 10 (*5*). The optical densities *D'* were measured with the use of a light filter with $\lambda_{max}$ = 450 nm.

It was demonstrated by special experiments that the quality of gelatin has no effect on complexation. Hence, it can be concluded that in the case under consideration, as in other known systems, *viz.*, in systems containing a metal ion and an (N,O,S)-donor chelating agent,[6] gelatin was not involved in complexation as a ligand. The analytical-grade and chemically pure reagents were used for the preparation of $Co_2[Fe(CN)_6]$-GIM and complexation without additional purification.

The optical density of metal-chelate GIM was measured by transmitted light (*D'*) on a Macbeth TD504 photometer in the range of 0.1—5.0 with an accuracy of ±2%. The electronic absorption spectra of immobilized matrix systems were recorded on a Specord UV-VIS spectrophotometer (Karl Zeiss, Germany) in the range of 400—800 nm; the *D'* values were determined with an accuracy of ±2% (rel.). The IR spectra were recorded on a UR-20 spectrometer (Karl Zeiss, Germany). The differential thermal analysis was carried out on a Paulik—Paulik—Erdey Q derivatograph (Hungary) at a rate of heating of 20 °C min$^{-1}$. The pH was measured using a pH-340 potentiometer with an accuracy of ±0.05 pH units. The ESR spectra were obtained on a Bruker ESR200D spectrometer (Germany) at 298 K. The kinetic curves $D' = f(C_f, C_l^0, t)$ were processed using the PTKDCGIM program.[10]

## Results and Discussions

Treatment of cobalt(II) hexacyanoferrate(II) GIM with an aqueous-alkaline solution of dithiooxamide and glyoxal (the concentration of dithiooxamide was $3.0 \cdot 10^{-3}$—$1.5 \cdot 10^{-2}$ mol L$^{-1}$ and the molar ratio of the reagents was 0.5—1.0) afforded a compound which turned the gelatin bulk to a dark-brown color. The visible region of the absorption spectrum of this GIM has no pronounced maxima (Fig. 4). When the reagents were taken in a molar ratio of no less than 2.0, a compound formed which turned the gelatin layer to an amber-yellow color. The absorption spectrum of this GIM also does not have distinct maxima (see Fig. 4). It is worthy of note that the spectral characteristics of "amber-yellow" GIM coincide with those for the $Co(HL)_3$ complex reported previously[1—3] (HL is the singly deprotonated form of dithiooxamide). This fact suggests that the redox process Co$^{II}$ → Co$^{III}$ occurred in the system under study. This is also evidenced by the fact that the coordination compounds

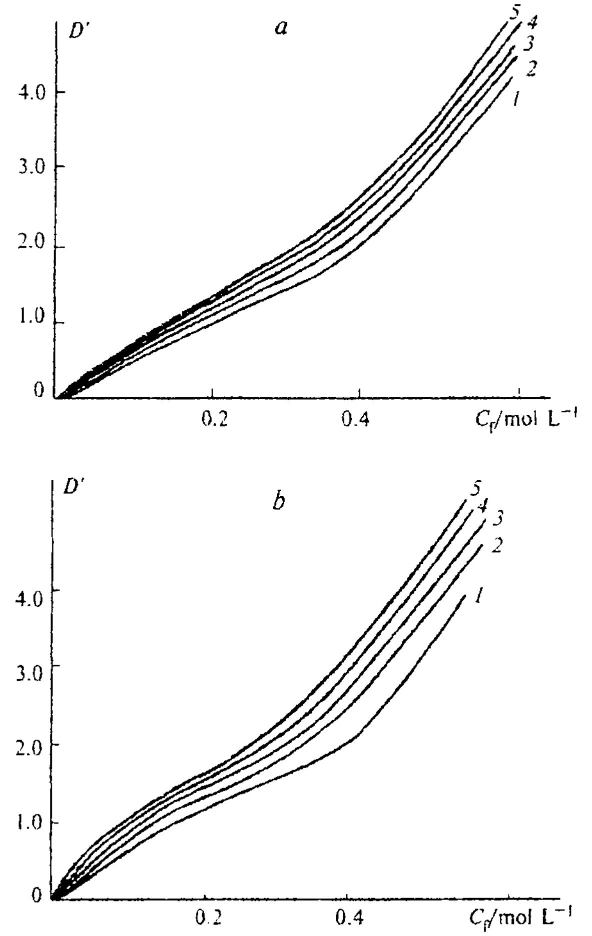


**Fig. 3.** Curves $D' = f(C_f, C_l^0, t)$ for the Co$^{II}$—dithiooxamide—glyoxal system in the coordination section ($C_l^0$ = const, variables $t$, and arguments $C_f$); the dithiooxamide : glyoxal ratio is 0.50 (*a*) and 1.00 (*b*). $C_l^0 = 1.2 \cdot 10^{-2}$ mol L$^{-1}$ and $t$/min = 1 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), and 10 (*5*). The optical densities $D'$ were measured with the use of a light filter with $\lambda_{max}$ = 450 nm.

which were formed in the Co$^{II}$—dithiooxamide—glyoxal system upon complexation in Co$_2$[Fe(CN)$_6$]-GIM and which were isolated from the corresponding metal-chelate GIM, are diamagnetic and do not exhibit ESR signals. This is possible only if these compounds contain Co$^{III}$ (rather than Co$^{II}$), which has a pseudooctahedral environment formed by the donor centers of the ligands.

The brown compound was formed in the matrix *only* upon interaction of Co$_2$[Fe(CN)$_6$]-GIM with aqueous-alkaline solutions containing *simultaneously* dithiooxamide and glyoxal. In the absence of the latter, the formation of any compound which turned the gelatin bulk to the brown color was not observed no matter what concentrations of dithiooxamide and Co$_2$[Fe(CN)$_6$] in the matrix were used. Apparently, both these organic compounds in the conditions under consideration are *simultaneously* involved in complexation. The dark-brown color of GIM may be associated either with the formation of heteroligand Co$^{III}$ coordination compounds containing dithiooxamide and glyoxal in the inner sphere or with the formation of Co$^{III}$ chelates with a new ligand, which is "assembled" from the above-mentioned ligands. Let us estimate the extent to which each of these alternatives is consistent with the experimental data.

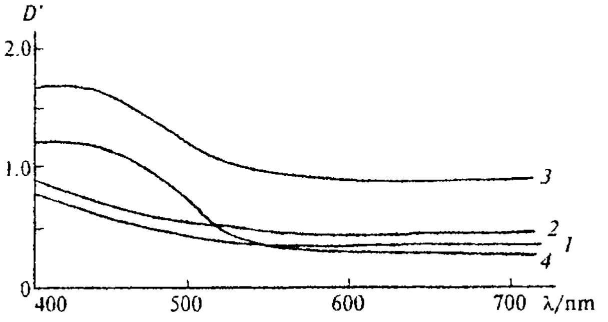
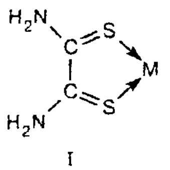
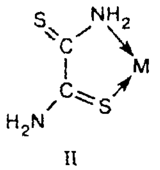


**Fig. 4.** Electronic absorption spectra of GIM with coordination compounds obtained in the Co$^{II}$—dithiooxamide—glyoxal system at $C_F$ = 0.19 mol L$^{-1}$, $C_l^0 = 3.0 \cdot 10^{-3}$ mol L$^{-1}$, and $t$ = 2 min; the ratio of the initial ligsons is 0.50 (curve *1*), 1.00 (*2*), and 2.00 (*3*); and in the Co$^{II}$—dithiooxamide system at $C_f$ = 0.38 mol L$^{-1}$, $C_l^0 = 1.2 \cdot 10^{-3}$ mol L$^{-1}$, and $t$ = 4 min (curve *4*).

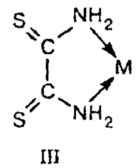
Dithiooxamide is an ambidentate ligand which can form five-membered rings with the participation of the (S,S), (N,S), or (N,N) donor centers. Of three theoretically possible modes of coordination of the metal ion (M) to this ligand (I—III), mode I can be excluded at once because Co$^{III}$ belongs to Pearson's hard acids and dithiooxamide should be coordinated to such ions through rather highly electrophilic atoms (in the case under consideration, through the N atom), *i.e.*, according to either mode II or III.



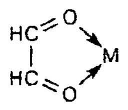
I



II



III

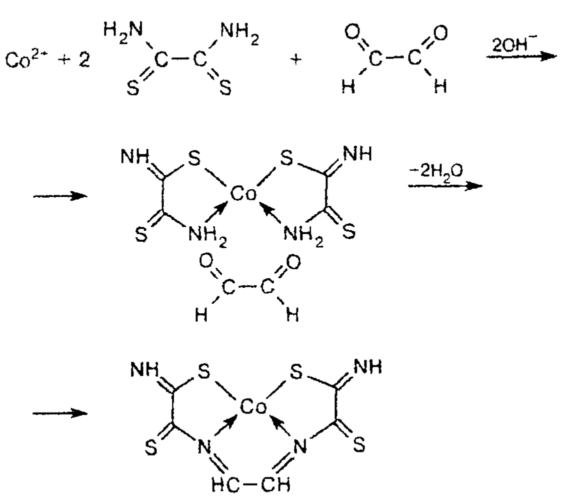


Glyoxal can, in principle, act as an (O,O)-donor bidentate ligand to form a five-membered metal ring upon complexation with Pearson's hard acids. On this basis and taking into account the facts that Co$^{III}$ adopts the coordination number of 6 and has an octahedral or pseudooctahedral environment almost without exception, it is believed that the first mode should lead either to heteroligand coordination compounds with a cobalt(III) ion : dithiooxamide : glyoxal ratio of 1 : 2 : 1 or 1 : 1 : 2 or to coordination compounds with a cobalt(III) ion : dithiooxamide : glyoxal ratio of 1 : 1 : 1 and two additional monodentate ligands, which complete the octahedral structure ($H_2O$ molecules and $OH^-$ anions are the most probable additional ligands). If it is assumed that a particular heteroligand complex is actually formed in the case under consideration, a *homoligand* $Co^{III}$ chelate containing *glyoxal* with a metal ion to glyoxal ratio of 1 : 2 or 1 : 3 would be expected to be formed in the presence of an excess of glyoxal with respect to dithiooxamide. This complex should differ in color both from the homoligand $Co^{III}$ chelate with dithiooxamide of 1 : 3 composition (amber-yellow[1—3]) and from any possible heteroligand chelate. In this case, the color of gelatin bulks should change from amber-yellow to dark-brown and then to another color as the concentration of glyoxal increases. However, this change in the color was not observed and the dark-brown color still persisted when the reagents were taken in a molar ratio substantially smaller than 0.5. Moreover, when $Co_2[Fe(CN)_6]$-GIM was treated with alkaline solutions of glyoxal, no changes in the spectral characteristics of GIM were observed, which indicates that $Co^{III}$ compounds with this organic ligand cannot be formed under the above-mentioned conditions. According to the data of chemical analysis of the compounds isolated from dark-brown GIM, all these compounds are one and the same chemical compound with the molecular formula $C_6H_7CoN_4S_4O_2$ (found (%): C, 20.4; H, 2.2; Co, 16.8; N, 15.8; S, 36.1; calculated for $C_6H_7CoN_4S_4O_2$ (%): C, 20.36; H, 1.98; Co, 16.63; N, 15.81; S, 36.19) regardless of the molar ratio of the concentrations of dithiooxamide and glyoxal. Our experiments demonstrated that none of the known[1—3] immobilized $Co^{III}$ chelates with dithiooxamide, which were formed upon complexation in cobalt(II) hexacyanoferrate(II) GIM, reacted with aqueous-alkaline solutions of glyoxal at any pH and glyoxal concentration used. The dark-brown compound was also not formed in the reaction of the only dithiooxamide-containing $Co(HL)_3$ chelate, which was obtained upon complexation in solution, with an aqueous-alkaline solution of glyoxal. Therefore, the suggested formation of heteroligand complexes is obviously contradictory to the experimental data and hence it can be concluded that a new ligand was formed in the system. Dithiooxamide and glyoxal serve as "building blocks" for this ligand.

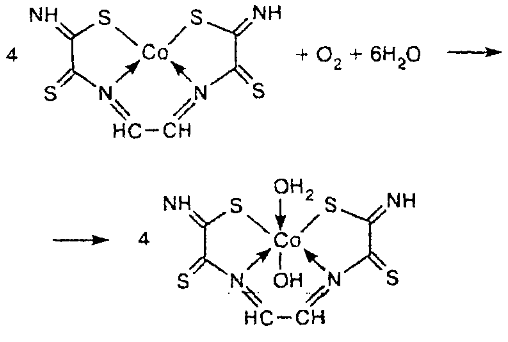
This "assembled" ligand was not formed when aqueous solutions of dithiooxamide and glyoxal were directly mixed, as evidenced by the fact that the absorption spectra of aqueous solutions of dithiooxamide are identical to those of aqueous solutions containing dithiooxamide and glyoxal at pH > 9.0. Consequently, this ligand can be formed only in the presence of the metal ion. This fact suggests that the template synthesis occurs in the $Co^{II}$—dithiooxamide—glyoxal system upon complexation in $Co_2[Fe(CN)_6]$-GIM. On this basis and taking into account the fact that atmospheric oxygen is the most probable oxidizing agent for the redox process $Co^{II} \rightarrow Co^{III}$, three pathways of this synthesis can be assumed.

1. The formation of a $Co^{III}$ coordination compound with a chelate ligand coordinated to the $Co^{III}$ ion through two N atoms and two S atoms. In this case, the ligand can be "assembled" from two dithiooxamide molecules and one glyoxal molecule according to Schemes 1 and 2.

**Scheme 1**

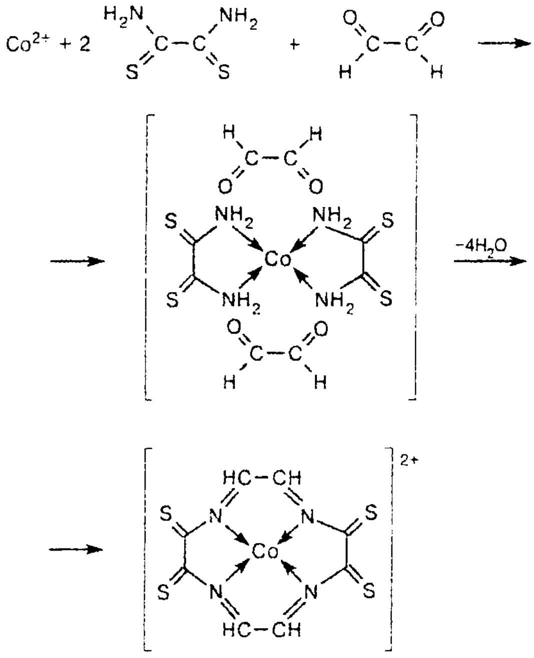


**Scheme 2**

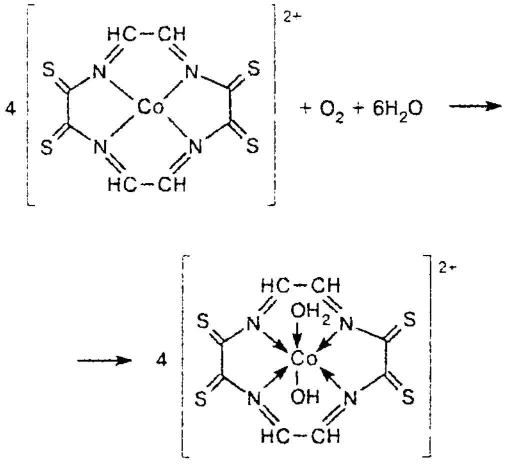


2. The formation of cobalt(III) complexes with a chelate ligand coordinated to $Co^{III}$ through four N atoms. The ligand is formed by two dithiooxamide molecules and two glyoxal molecules. In this case, as in the first case, the resulting complex contains $H_2O$ molecules

**Scheme 3**



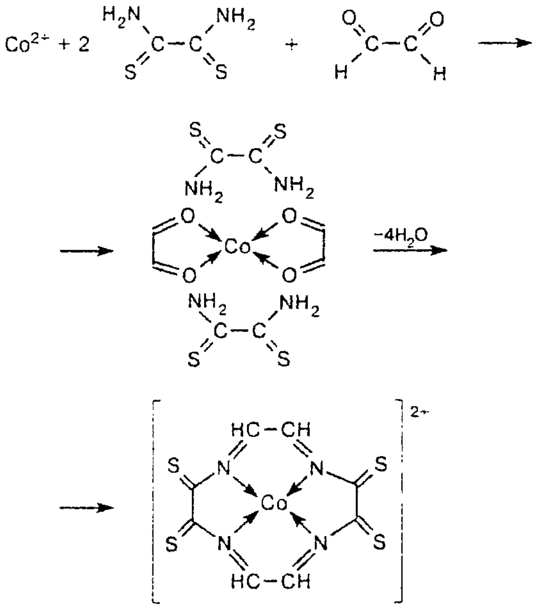
**Scheme 4**



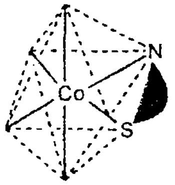
and $OH^-$ ions along with the above-mentioned ligand in the inner coordination sphere (Schemes 3 and 4).

3. The formation of a cobalt(III) coordination compound with a chelate ligand coordinated to $Co^{III}$ through four N atoms. In this case, the ligand is also "assembled" from two dithiooxamide molecules and two glyoxal molecules, but $Co^{III}$ is coordinated by glyoxal, while dithiooxamide acts as a "linking" fragment (Scheme 5).

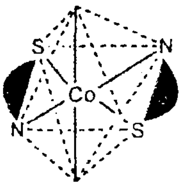
**Scheme 5**



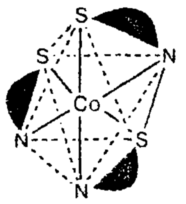
The complex obtained as a result of this "linking" completely coincides with that obtained according to Scheme 3 and consequently the final complexes formed according to pathways 2 and 3 also coincide with each other. However, both pathways afford a cationic complex, which involves either $[Fe(CN)_6]^{4-}$ or $OH^-$ as the counterion. In the first case, the complex, which is formed in GIM, should contain iron. In the second case, the complex should contain at least three O atoms per Co atom, which was not in fact observed. Only the complex formed according to Schemes 1 and 2 has a molecular formula which exactly coincides with that of the chemical compound isolated from the dark-brown GIM. Analysis of the dependences $D' = f(C_f, C_l^0, t)$ according to a known procedure[8,9] demonstrated that the reaction proceeds with the participation of one molecule of the "assembled" ligand, which is composed of two dithiooxamide molecules and one glyoxal molecule per $Co^{II}$ ion (the calculated stoichiometric coefficients for the metal ion and the ligand are 1.2 and 1.4, respectively). At the same time, computer simulation of complexation (according to the published data[8,9]), which was carried out on the assumption that the ligand is constructed from another set of ligsons (*viz.*, from two dithiooxamide molecules and two glyoxal molecules, two dithiooxamide molecules and three glyoxal molecules, *etc.*), gave the numbers of coordinated "assembled" ligands, which contradict both the chemical notion and the view of the coordination possibilities of $Co^{II}$ and $Co^{III}$. These data of mathematical analysis are consistent only with a combination of Schemes 1 and 2 and, consequently, with the mode of coordination of the macrocylic ligand through the (N,N,S,S) donor atoms. In this case, the N and S atoms should be in *cis* positions with respect to each other to prevent steric hindrance to the formation of the macrocyclic compound. The postulated structure of this coordination compound formed in the dark-brown GIM gives an insight into the reasons for the fact that this compound is not formed in the reaction of a particular dithiooxamide cobalt(II) complex with glyoxal either in solutions or in GIM. According to the published data,[2,3] complexation in the $Co^{III}$—dithiooxamide system in cobalt(II) hexacyanoferrate(II) GIM afforded three compounds of compositions $[Co(HL)]_4[Fe(CN)_6]_2$, $[Co(HL)_2]_4[Fe(CN)_6]$, and $[Co(HL)_3]$ with structures **A**, **B**, and **C**, respectively (the hatched segments arbitrarily represent singly deprotonated dithiooxamide molecules $HL^-$). For the first complex (**A**), template synthesis is in principle impossible because for this to happen, the structure of the starting $Co^{III}$ compound must contain at least two dithiooxamide molecules. For the second complex (**B**), template synthesis does not occur for steric reasons because the ligand molecules in this complex are in *trans* orientations with respect to each other and they cannot be linked through glyoxal molecules in the plane.[2,3] In the case of the third complex (**C**), this linking is also sterically hindered.



**A**



**B**



**C**

The IR spectra of the dark-brown complex has a broad band in the region of 3400—3600 $cm^{-1}$, which is characteristic of noncoordinated NH or $NH_2$ groups. Apparently, at least some N atoms in this compound are not coordinated to $Co^{III}$ and the resulting compound cannot have the structure formed according to Schemes 3—5. The coordination compounds formed in the latter cases could not contain NH or $NH_2$ groups. The spectrum has a band at 700 $cm^{-1}$, which belongs to $\nu(C=S)$.[11] Consequently, at least some S atoms are not bound to $Co^{III}$, which agrees with the structure of the complex postulated by us and formed according to Schemes 1—2. Unfortunately, the IR spectral patterns at $\nu < 1000$ $cm^{-1}$, where $\nu$(Co—N) and $\nu$(Co—S) should be manifested (see Ref. 9), did not allow us to unambiguously assign the observed bands to stretching vibrations of the Co—N and Co—S bonds. Finally, the IR spectrum of the dark-brown complex has a $\nu$(Co=N) band at 1640 $cm^{-1}$, which is also in complete agreement with the suggested structure.

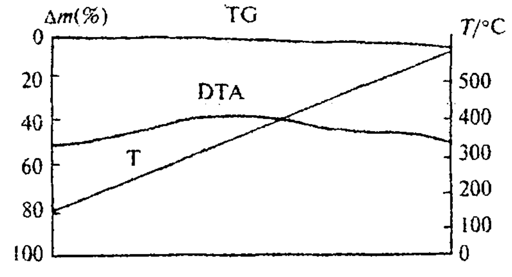
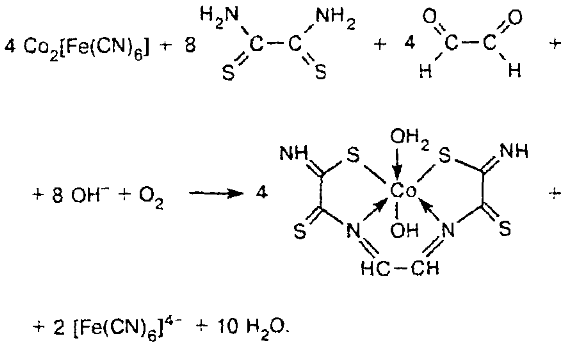


**Fig. 5.** Derivatogram of ((2,7-dithio-3,6-diaza-3,5-dithioamido-1,8)aquahydroxo)cobalt(III).

Taking into account the theoretical reasoning and the available experimental data, it can be concluded that the template synthesis occurs in the $Co^{II}$—dithiooxamide—glyoxal system under specific conditions of complexation in $Co_2[Fe(CN)_6]$-GIM. This synthesis is accompanied by oxidation of $Co^{II}$ to $Co^{III}$ with molecular oxygen and proceeds according to the following overall equation:



The compound which was isolated from GIM after completion of the reaction, *viz*., ((2,7-dithio-3,6-diaza-3,5-dithioamido-1,8)aquahydroxo)cobalt(III), is virtually insoluble in ethanol, acetone, chloroform, benzene, and teterachloromethane and poorly soluble in dimethylformamide, dimethyl sulfoxide, and hexamethylenephosphoramide. The electronic absorption spectrum of a dimethyl sulfoxide solution of the compound isolated from GIM is identical to that of the polymeric layer of the matrix, in which the compound under study was immobilized. This fact confirms that the compound in GIM and that isolated from GIM are one and the same substance. It should be noted that the resulting compound is very high-melting and does not undergo pyrolysis even at 600 °C. At 450 °C, an insignificant weight loss (~2%) was observed. The peak in the derivatogram (Fig. 5) does not correspond to the characteristic peaks of phase transitions. This is additional indirect evidence that the synthesized compound is actually a $Co^{III}$ coordination compound with the macrocyclic ligand.

We failed to obtain reliable structural data for the dark-brown compound isolated from GIM by X-ray diffraction analysis because the procedure for the isolation of this compound from matrix systems, which was used in this work and in previous studies,[1–3,7,10] afforded very small crystals unsuitable for X-ray study.

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