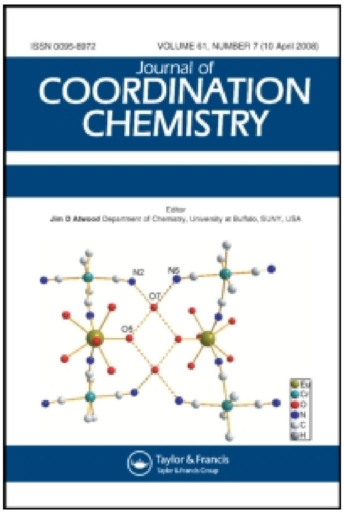

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Gelatin-immobilized metal complexes: synthesis and applications

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To cite this Article Mikhailov, Oleg V.(2008) 'Gelatin-immobilized metal complexes: synthesis and applications', Journal of Coordination Chemistry, 61: 9, 1333 — 1384
To link to this Article: DOI: 10.1080/00958970701579282
URL: http://dx.doi.org/10.1080/00958970701579282

Journal of Coordination Chemistry
Vol. 61, No. 9, 10 May 2008, 1333–1384

Gelatin-immobilized metal complexes: synthesis and applications

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(*Received 1 December 2006; in final form 30 April 2007*)

Formation of *p*-, *d*- and *f*-metal complex gelatin-immobilized matrix systems using reactions of electrophilic, nucleophilic substitution and template synthesis, and employment of these materials in photographic processes, in spectroscopy and for absorption of metal ions, have been summarized and discussed. The review covers the period 1990–2005.

Keywords: Metal complex; Gelatin-immobilized matrix; Electrophilic substitution; Nucleophilic substitution; Template synthesis; Hexacyanoferrate(II)

1. Introduction

A new direction in materials science is the study of chemical processes proceeding in metal-containing immobilized systems that are distinguished by their ability to immobilize the starting reagents and reaction products in the polymer. Such immobilization, in principle, can be achieved: (*a*) by a chemical reaction with the use of the functional groups of the relevant polymer; and (*b*) by means of intermolecular forces. The immobilized systems of type (*a*) first drew investigators' attention, owing to their wide use in metal complex catalysis [1–6]. Metal complex catalysis and organic synthetic reactions on polymer supports [7–10] remain the main applications of immobilized metal-containing matrix materials [1, 3, 5] although one has to note that the range of applications and their potential possibilities is much greater [11–20]. Moreover, the wide practical use of materials of such a type has stimulated a series of specialized scientific conferences devoted to problems of synthesis and application of polymer-immobilized matrix materials. The content of these conferences led to special issues of such scientific journals as *Journal of Molecular Catalysis* [21, 22] and *British Polymer Journal* [23].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701579282

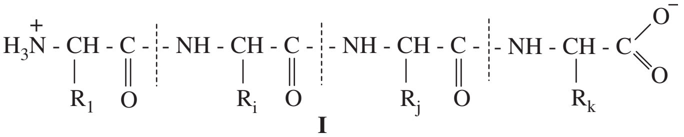
The analysis of literature data allow us to conclude that metal-containing immobilized matrix materials of type (*a*) and chemical processes in them have been fairly well studied by now. Metal-containing immobilized materials of type (*b*) and chemical processes in them, including complexation reactions, however, have not received proper attention. It should be noted in this connection that gelatin-immobilized systems rather widely are employed in biochemistry (see, for example, [24–33]).

The most common and interesting of such systems are the so-called metal complex gelatin-immobilized matrix materials which can be easily synthesized from starting AgHal-gelatin-immobilized matrix systems (which actually are nothing but light-sensitive layers of modern silver halide photographic materials). These systems may be readily transformed by using standard procedure [34, 35] into Ag-gelatin-immobilized matrices containing silver particles comparable in size to large clusters. In its turn, Ag-gelatin-immobilized matrix materials may be used as a starting substance from which one can obtain, via specific reactions, the gelatin-immobilized matrix materials with a wide range of immobilized chemical compounds that will maintain the quasi-molecular level of particle dispersity which was already reached for silver-containing matrix materials.

The goal of this work was to generalize the problems of synthesis and practical application of *p*-, *d*- and *f*-metal complex gelatin-immobilized matrix systems and materials based thereon.

2. Gelatin as polymer massif

Gelatin is known to be a polydisperse mixture of relatively low-molecular-mass polypeptides having general formula **I** (R_1, R_i, R_j, R_k – various radicals) and molecular mass $M_{Gel} = (2.0–3.0) \cdot 10^5$ [34–39].



$$H_3\overset{+}{N}-\underset{\underset{R_1}{|}}{CH}-\underset{\underset{O}{\|}}{C}-\vdots-NH-\underset{\underset{R_i}{|}}{CH}-\underset{\underset{O}{\|}}{C}-\vdots-NH-\underset{\underset{R_j}{|}}{CH}-\underset{\underset{O}{\|}}{C}-\vdots-NH-\underset{\underset{R_k}{|}}{CH}-C\genfrac{}{}{0pt}{}{\diagup O^-}{\diagdown\!\!\diagdown O}$$

I

The structure and properties of these biopolymers were studied (see, for example, [34–54]). Amino acid composition of gelatin is shown in figure 1.

Molecules of this high-molecular weight compound consist of three α-type polypeptide chains with almost identical molecular masses, two α-chains usually being almost identical with respect to the set and sequence of the aminoacids (α1-chain) while the third (α2-chain) differs from the other two [40, 41, 45]. A structure has been proposed for such molecules in which a left-handed helical structure of the α-type was attributed to each polypeptide chain [42, 43, 45]. Within the framework of such a structure, all three helices are plaited with each other to form a single right-handed helix; hydrogen bonds play a significant role in this stabilization [42]. The α2-chains are characterized overall by the same set of polypeptide fragments as the α1-chains, but their aminoacid sequence contains fewer aminoacids such as proline, hydroxyproline and lysine, the predominating aminoacids being tyrosine, valine, leucine, histidine

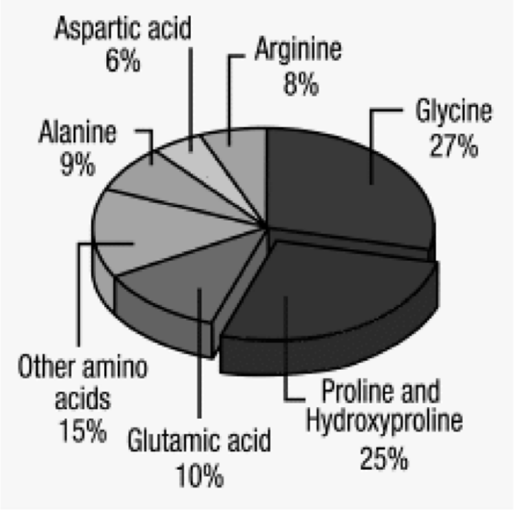


Figure 1. Amino acid composition of gelatin [50].

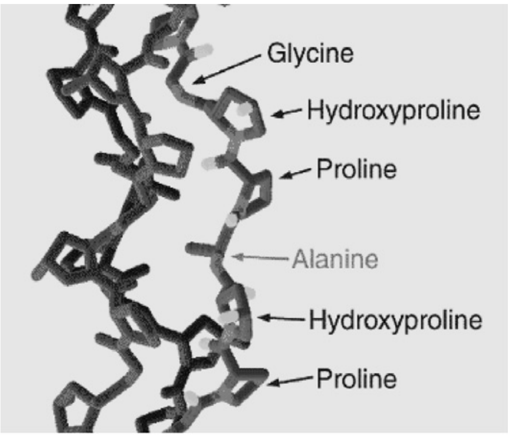
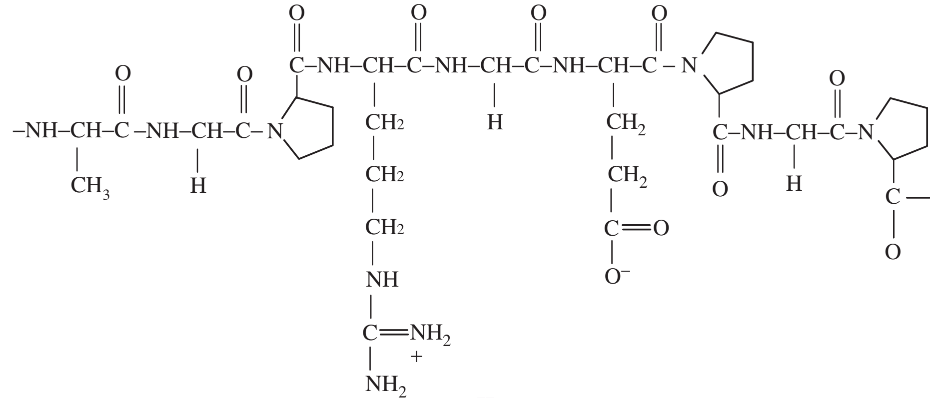


Figure 2. Three polypeptide α-chains form a triple-helix of gelatin. Gelatin is stabilized by the formation of covalent cross-links, both within the gelatin triple helix and between gelatin helices [45].

and hydroxylysine [35]. The sequence of the peptide fragments in the α1-chains with more than 700 amino acid residues has been fully elucidated [34, 35, 50]. The structure of gelatin is shown in figure 2.

A typical structural fragment of gelatin is –Ala–Gly–Pro–Arg–Gly–Glu–4Hyp–Gly–Pro (**II**). In contrast to other proteins, where common features in the alternation of the aminoacids in the peptide fragments have not been found, in gelatin, starting with the 17-th residue, glycine invariably occupies each third position so that the overall formula of the polypeptide units in the α1-chain may be written as Gly–A–B, where Gly is glycine, A and B are other aminoacid residues, most frequently encountered are

Gly–Pro–Hyp combination [35, 50]. The sequence of the aminoacid residues in the α2-chain is not accurately established up to now.



II

Like other proteins, gelatin is an ampholyte owing to free acid and basic groups (i.e. groups which can be titrated in aqueous solutions) such as the β-carboxy group of aspartic acid, the β-carboxy group of glutamic acid, the β-imidazol group of histidine, the δ-guanidino group of arginine, the ε-amino group of lysine and the phenolic hydroxy group of tyrosine [35]. Their nitrogen and oxygen atoms play the role of donor centers in relation to various *p*-, *d*- and *f*-element ions but, overall, gelatin is a fairly weak complex-forming agent [34, 35, 50].

Gelatin masses resemble a rubber in elastic properties; this is quite natural for infinite chains formed by long chains of molecules connected by a limited number of cross links [44, 48, 50, 51]. Such a structure is potentially suitable for formation of polymer-immobilized matrix materials; it permits the formation of no rigid crystalline blocks and furthermore contains a fairly large number of cells for the reception and subsequent fixation of the molecules of the immobilized substance. When filled with molecules of corresponding compound, these cells retain a certain freedom of migration in space. With a polymer of such a structure, it may be possible, in principle, to obtain immobilized matrix systems characterized by a fairly uniform distribution of metal-containing compounds in some part of the polymer massif. In addition, such immobilized matrices are sterically accessible for the occurrence of diverse chemical processes, especially complexing reactions. Gelatin has an extremely high surface area and an extensive system of micropores so that when it comes into contact with aqueous solution, the permeation of both the solvent molecules and of the solute into polymer massif occurs comparatively readily [34, 35, 45–54]. Polymer layers in the gelatin exhibit isotropic physical and mechanical parameters and are transparent, hydrophilic, and plastic.

3. Synthesis of metal complex gelatin-immobilized matrix materials

3.1. *Main principles*

Nearly all of the work dealing with complexing in similar matrix systems involves 3*d*-metal hexacyanoferrates(II) which display the required level of hardness of fixation in the gelatin mass, optimal kinetic lability, stability, and sufficiently low solubility in water. The peculiarity of complexing in the metal hexacyanoferrate(II) gelatin-immobilized matrices is that it occurs when some of the above matrices come into contact with a solution (aqueous, as a rule) of the relevant ligand. Taking into account a summary of the data on gelatin as polymer material [34–37] and the topography of the obtained immobilized matrix systems, one can distinguish the following specific details of complexing under given conditions [55, 56]:

- hampered contact between reagents;
- availability of charge on the polymer in contact with the ligand solution (since gelatin is known to be an ampholyte [34–37]);
- the reaction volume is extremely small;
- low rate of delivery of the ligand into polymer mass;
- nonuniformity of the complexation process.

It is obvious that complexing in the metal hexacyanoferrate(II) matrix-ligand solution systems should be regarded as a specific phenomenon which can be described by a model different from that used for treating complexing in a solution and a solid phase. The methodological principles of such a model were set forth [56, 57]. Although these are typical heterogeneous systems, complexing therein may be considered quasi-homogeneous since it occurs not at the solid/liquid interface (matrix/ligand solution), but in the volume of the polymer layer of the matrix. Every such matrix represents a reaction microvolume which is in the solid phase, and the reagents of the chemical reaction (in particular, complexation) enter this volume by means of diffusion from a solution that is in contact with it. The reactive substance of metal hexacyanoferrate(II) matrix is in the gelatin mass in the form of an interlayer 10–20 µm thick with a 5–15 µm gelatin layer above [55–57]. The particles of this compound may be regarded to a good approximation as coordination polymers with a relatively small molecular weight and a sufficiently regular structure enclosed in the voids between the polypeptide chains of gelatin molecules (figure 3). Metal hexacyanoferrate(II) coordination polymers usually have a face-centered cubic lattice; Fe(II) has coordination number six and an octahedral environment, whereas other incorporated *d*-metals have coordination numbers four or six and tetrahedral or octahedral coordination, respectively [58]. In all cases, Fe(II) coordinates CN^- groups through the carbon atom and coordinates M (M is a metal ion) through the nitrogen atom [58]. When a metal hexacyanoferrate(II) matrix comes into contact with the ligand solution, the ligand diffuses into the polymer mass where it reacts with the corresponding hexacyanoferrate(II) and binds M into a new more stable (as compared to metal hexacyanoferrate(II)) complex, as a result of which the M–N bonds break. The obtained kinetically inert $[Fe(CN)_6]^{4-}$ anion is removed from the matrix into the ligand solution. Thus, the metal hexacyanoferrate(II) concentration in the matrix gradually decreases in the course of complexation. On the contrary, the ligand concentration in the polymer layer continuously grows due to its migration from the solution into the polymer and is only limited by the diffusion factors and its concentration in the solution.

By considering the above features of complexing in the metal hexacyanoferrate(II) gelatin-immobilized matrix, one can predict formation and accumulation in the

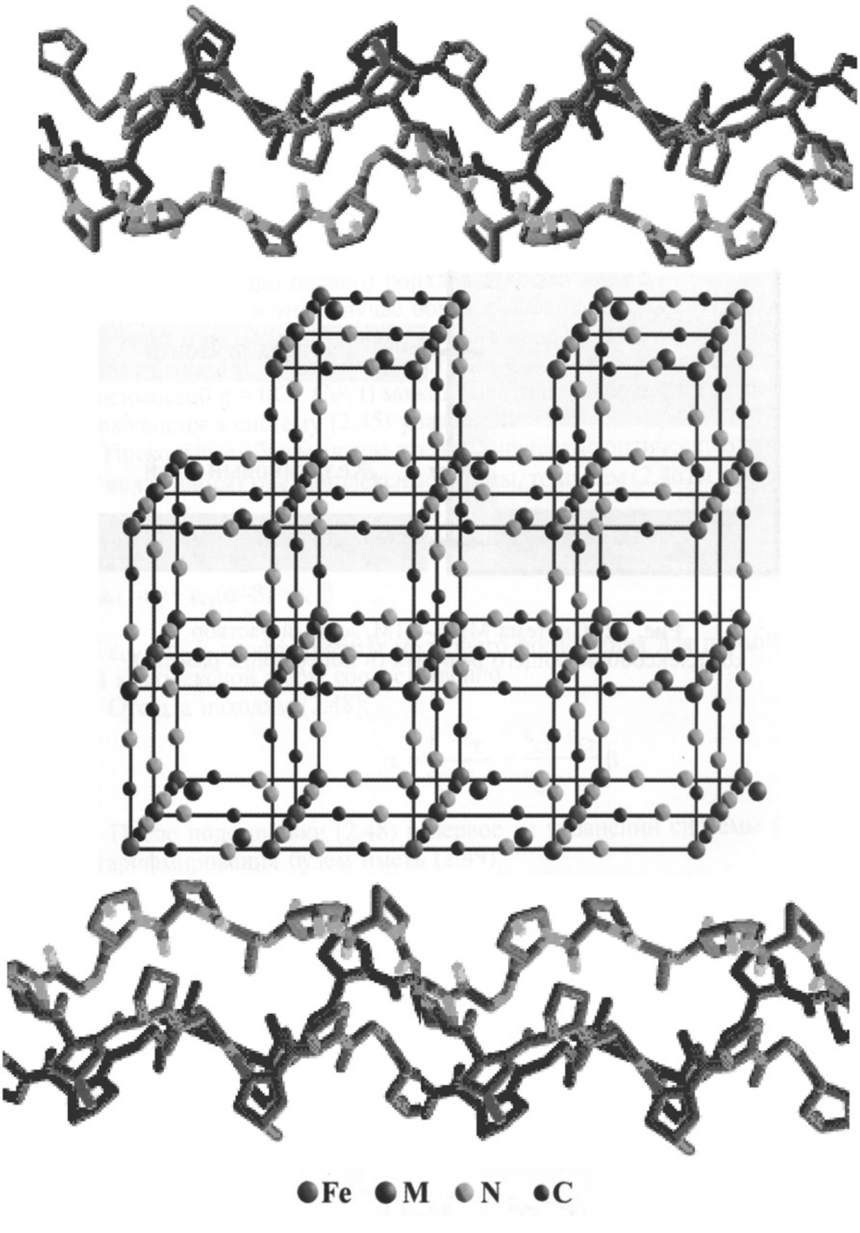


Figure 3. The structure of metal hexacyanoferrate(II) gelatin-immobilized matrix [55].

immobilized matrix of the following types of coordination compounds that are not typical for complexing in solution [55–57]:

- intermediate complex forms;
- the so-called ligand-deficient complexes, where the number of the ligand coordinated molecules is less than the number which corresponds to the coordination saturation of the central M atom with respect to this ligand;

- coordination dimers and polymers;
- chelate complexes with an extent of ligand deprotonation that is not typical for the solutions (proton-deficient complexes).

The polymer binder of metal hexacyanoferrate(II) immobilized matrix-gelatin can, in principal, act as a chelating ligand. Nevertheless, in our case, gelatin does not react with metal hexacyanoferrate(II) because the stability of its coordination compounds with the M ions is much lower than that of the hexacyanoferrates(II) of corresponding metal ions. If hexacyanoferrate(II) of a certain M can interact with some other ligand while gelatin does not react with this ligand, then gelatin will not react as a ligand with the metal complex product of the complexing reaction either [55, 56]. The following can be assumed: first, ligand diffusion to the metal hexacyanoferrate(II) matrix reaction volume is not attended by any chemical reaction and, second, the solid/solution interface does not influence complexing in the system.

The complexing in the metal hexacyanoferrate(II) gelatin-immobilized matrix-ligand solution system may be described by a mathematical tool of the so-called external task of diffusion kinetics in combination with the classic kinetic equations of the Guldberg-Waage principle [55, 56]. An increase in the solubility of the metal-containing component of the matrix in water facilitates diffusion into the solution and, thus, the destruction of the matrix by this solution. For this reason, in most cases, the complexation of metal hexacyanoferrate(II) with chelating ligands was studied under conditions with poorly soluble coordination compounds formed in the matrix, i.e. in the alkaline medium at $pH > 9$.

Complexation in metal hexacyanoferrate(II) gelatin-immobilized matrix can theoretically follow the same two mechanisms as complexing in a solution or solid phase [59]. The first mechanism is the classical associative S_N2 mechanism, while the second is partially analogous to the classical dissociative S_N1 mechanism of nucleophilic substitution of the ligands (pseudo-S_N1-mechanism) [56, 60–62]. In the first variant, metal hexacyanoferrate(II) is stable to OH^- ions and $[Fe(CN)_6]^{4-}$ is eliminated by stages; the rate of complexation is limited by a bimolecular reaction. In the second one, metal hexacyanoferrate(II) undergoes alkaline destruction to give the corresponding oxide or oxohydroxide, as occurs in $Cu_2[Fe(CN)_6]$ or $KFe[Fe(CN)_6]$ according to equations (1), (2), and (3),

$$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-} \tag{1}$$

$$KFe[Fe(CN)_6] + 2OH^- \rightarrow Fe(OH)_2 + [Fe(CN)_6]^{3-} + K^+ \tag{2}$$

$$KFe[Fe(CN)_6] + 3OH^- \rightarrow FeO(OH) + [Fe(CN)_6]^{4-} + K^+ \tag{3}$$

which becomes a launching site for the realization of the interaction between the M ion and the ligand. In this case, on one hand, the rate of formation of the oxohydroxide depends on the metal hexacyanoferrate(II) concentration in the matrix but is independent of the ligand concentration in solution, which shows an obvious analogy with typical dissociative processes; on the other hand, the rate of complexation proper is also limited here by the bimolecular reaction which is typical of the associative processes [59]. The overall equations of the chemical reactions for each of these mechanisms and the equations for analysis of experimental kinetic curves $D^{\blacktriangledown} = f(C_F, C_R^{\circ}, t)$, where $D^{\blacktriangledown}$ is the optical density of the gelatin-immobilized matrix formed as a result of complexation, C_F is the volume concentration of the hexacyanoferrate(II) to the metal ion in the starting metal hexacyanoferrate(II) matrix, C_R° is the concentration of electrophilic or nucleophilic reagent in the solution contacting the matrix, and t is the contact time, have been presented [55, 56].

In available publications on the problems of complexing in the metal hexacyanoferrate(II) matrix one can outline three main subjects: reactions of electrophilic substitution, nucleophilic substitution and template synthesis.

3.2. *Electrophilic substitution in metal hexacyanoferrate(II) gelatin-immobilized matrices*

Generally, the reactions of such a type (ionic exchange) may be written by equation (4) for the metal hexacyanoferrates(II), $M_2[Fe(CN)_6]$, equation (5) for $M_4[Fe(CN)_6]_3$ and equation (6) for $M[Fe(CN)_6]$ composition (m, n, r, s – whole numbers):

$$\begin{aligned}4mM_2[Fe(CN)_6] + 4n\mathbf{M}^{k+} \rightarrow\ & M_{8m-40s}\mathbf{M}_{4n}[Fe(CN)_6]_{nk+4m-2s} + 4sM^{2+}\\ & + (2s - nk)[Fe(CN)_6]^{4-}\end{aligned} \tag{4}$$

$$\begin{aligned}4mM_4[Fe(CN)_6]_3 + 4n\mathbf{M}^{k+} \rightarrow\ & M_{16m-4s}\mathbf{M}_{4n}[Fe(CN)_6]_{nk+12m-3s} + 4sM^{3+}\\ & + (3s - nk)[Fe(CN)_6]^{4-}\end{aligned} \tag{5}$$

$$\begin{aligned}4mM[Fe(CN)_6] + 4n\mathbf{M}^{k+} \rightarrow\ & M_{4m-4s}\mathbf{M}_{4n}[Fe(CN)_6]_{nk+4m-4s} + 4sM^{4+}\\ & + (4s - nk)[Fe(CN)_6]^{4-}\end{aligned} \tag{6}$$

Metal ion substitutions are possible and should be typical in metal hexacyanoferrate(II) gelatin-immobilized matrices, but the available data on this subject is very scarce. The first description [63] of substitution of Ag(I) for Co(II) in the $Ag_4[Fe(CN)_6]$-matrix, overall reaction (7) (with immobilized compounds given in braces {...}),

$$\{Ag_4[Fe(CN)_6]\} + 2CoCl_2 \rightarrow \{Co_2[Fe(CN)_6] + 4AgCl\} \tag{7}$$

was used to synthesize gelatin-immobilized hexacyanoferrate(II) Co(II). It was shown [63, 64] that halides of *p*-, *d*-, and *f*-elements in different oxidation states can be used to perform electrophilic substitution in the $Ag_4[Fe(CN)_6]$ matrix. The processes that occur in this case can be approximated by equations (8)–(10) (Hal = Cl, Br):

$$\{Ag_4[Fe(CN)_6]\} + 2MHal_2 \rightarrow \{M_2[Fe(CN)_6] + 4AgHal\} \tag{8}$$

$$(M = VO, Mn, Fe, Co, Ni, Cu, Zn, ZrO, Cd, UO_2)$$

$$3\{Ag_4[Fe(CN)_6]\} + 4MHal_3 \rightarrow \{M_4[Fe(CN)_6]_3 + 12AgHal\} \tag{9}$$

$$(M = V, Fe, Bi, Ce, Nd, Tl)$$

$$\{Ag_4[Fe(CN)_6]\} + MHal_4 \rightarrow \{M[Fe(CN)_6] + 4AgHal\} \tag{10}$$

$$(M = Ti, Sn, Th)$$

The electrophilic substitution reactions described above extend the range of the metal hexacyanoferrate(II) gelatin-immobilized matrix systems (both homo- and heteronuclear ones) and thus increases the number of *p*-, *d*-, and *f*-elements that can be used for carrying out complexation in the gelatin-immobilized matrices.

In spite of the fact that chemistry of hexacyanoferrates(II) was 300 years old in 2004, interest in such coordination compounds remains high; the evidence of it are the numerous publications of the last 20–25 years [65–84]. Although first reports concerning formation of (*dd*)heteronuclear metal hexacyanoferrates(II) of Cu(II) appeared in 1938 [85], reactions of their formation began to be studied in detail recently [86–104]. Attempts to synthesize heteronuclear metal hexacyanoferrates(II) using the interaction between $Mn_2[Fe(CN)_6]$-gelatin-immobilized matrix and water solutions of chlorides of 3*d*- and 4*d*-elements, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ and $CdCl_2$ [86, 87], between $Co_2[Fe(CN)_6]$-matrix and water solutions of $MnCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ and $CdCl_2$ [88–90], between $Ni_2[Fe(CN)_6]$-matrix and water solutions of $MnCl_2$, $CoCl_2$, $CuCl_2$, $ZnCl_2$ and $CdCl_2$ [91, 92], between $Cu_2[Fe(CN)_6]$-matrix and water solutions of $MnCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$ and $CdCl_2$ [93–95], between $Zn_2[Fe(CN)_6]$-matrix and water solutions of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $CdCl_2$ [96–98], and between $Cd_2[Fe(CN)_6]$-matrix and water solutions of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ [99–101], were undertaken. Indeed, (NiCo)–, (NiCu)–, (NiZn)–, (NiCd)–, (CuCo)–, (CuNi)–, (CuZn)– and (CuCd)heteronuclear hexacyanoferrate(II) (table 1) are formed (among their number, $Ni_{13}Co_3[Fe(CN)_6]_8$, $Ni_{11}Zn_5[Fe(CN)_6]_8$, $Cu_{11}Co_5[Fe(CN)_6]_8$, $Cu_{13}Cd_3[Fe(CN)_6]_7(CN)_4$). IR spectra of heteronuclear metal hexacyanoferrates(II) show extreme displacement of maxima of bands ν(CN), ν(Fe–C) and δ(Fe–CN) in comparison with corresponding mononuclear hexacyanoferrates(II) $M_2[Fe(CN)_6]$ and $M'_2[Fe(CN)_6]$ [86, 88, 91, 94, 96, 99, 102]. Examples of $D^{\blacktriangledown} = f(C_F, C^{\circ}_M, t)$ relationships where C°_M is a metal ion in solution contacting with matrix, have been presented in figure 4.

Three facts attract attention: first, for all couples (M/M′) in table 1 (with the exception of (M/Mn) couple), electrophilic substitution process occurs in the $\{\mathbf{M_2[Fe(CN)_6]}\}$– $M'Cl_2$ system as well as in the $\{\mathbf{M'_2[Fe(CN)_6]}\}$–$MCl_2$ system. In each system indicated only *one* (*dd*)heteronuclear hexacyanoferrate(II) is formed. Secondly, the compositions of (*dd*)heteronuclear hexacyanoferrates(II) formed in the $M_2[Fe(CN)_6]$–$M'Cl_2$ and $M'_2[Fe(CN)_6]$–MCl_2 systems (with the exception perhaps only of (Cu/Zn) couple) **are not identical** (for example, $Co_7Zn_{25}[Fe(CN)_6]_{16}$ in the $\{\mathbf{Co_2[Fe(CN)_6]}\}$–$ZnCl_2$ system [88] and $Zn_{13}Co_{19}[Fe(CN)_6]_{16}$ in the $\{\mathbf{Zn_2[Fe(CN)_6]}\}$–$CoCl_2$ system [66]). Third, the *full* electrophilic substitution according to equation (11) or (12)

$$\{\mathbf{M_2[Fe(CN)_6]}\} + M'Cl_2 \rightarrow \{\mathbf{M'_2[Fe(CN)_6]}\} + MCl_2 \tag{11}$$

$$\{\mathbf{M_2'[Fe(CN)_6]}\} + MCl_2 \rightarrow \{\mathbf{M_2[Fe(CN)_6]}\} + M'Cl_2 \tag{12}$$

does not occur. Formation of any compound in table 1 occurs at the contact of $M_2[Fe(CN)_6]$ with $M'Cl_2$ and $M_2[Fe(CN)_6]$ with $M'Cl_2$, neither in solution nor in solid phase. The processes of electrophilic substitution in $\{\mathbf{M_2[Fe(CN)_6]}\}$–$FeCl_3$ and $\{\mathbf{Fe_4[Fe(CN)_6]_3}\}$–$MCl_2$ systems (M = Mn, Co, Ni, Cu, Zn, Cd) have been studied [102–104]. As in the $\{\mathbf{M_2[Fe(CN)_6]}\}$–$M'Cl_2$ systems, formation of metal hexacyanoferrates(II) having specific composition occurs in this case (table 2).

Table 1. Heteronuclear(*dd*) metal hexacyanoferrates(II) forming as a result of electrophilic substitution (ionic exchange) reactions in the **{$M_2[Fe(CN)_6]$}**–$M'Cl_2$ systems into $M_2[Fe(CN)_6]$-gelatin-immobilized matrix materials [55].

	Ion of substituting M(II)					
Matrix **$M_2[Fe(CN)_6]$**	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
$Mn_2[Fe(CN)_6]$	■	$Mn_9Co_7[Fe(CN)_6]_8$	$Mn_3Ni_{61}[Fe(CN)_6]_{32}$	$Mn_2Cu_{14}[Fe(CN)_6]_8$	$MnZn_{15}[Fe(CN)_6]_8$	$Mn_{41}Cd_{23}[Fe(CN)_6]_{32}$
$Co_2[Fe(CN)_6]$	–	■	$Co_{17}Ni_{15}[Fe(CN)_6]_{16}$	$Co_4Cu_{28}[Fe(CN)_6]_{16}$	$Co_7Zn_{25}[Fe(CN)_6]_{16}$	$Co_9Cd_{55}[Fe(CN)_6]_{16}$
$Ni_2[Fe(CN)_6]$	–	$Ni_{13}Co_3[Fe(CN)_6]_8$	■	$Ni_{11}Cu_5[Fe(CN)_6]_8$	$Ni_{11}Zn_5[Fe(CN)_6]_8$	$Ni_{12}Cd_3[Fe(CN)_6]_7(CN)_2$
$Cu_2[Fe(CN)_6]$	–	$Cu_{11}Co_5[Fe(CN)_6]_8$	$Cu_{23}Ni_9[Fe(CN)_6]_{16}$	■	$Cu_{13}Zn_3[Fe(CN)_6]_8$	$Cu_{13}Cd_3[Fe(CN)_6]_7(CN)_4$
$Zn_2[Fe(CN)_6]$	–	$Zn_{13}Co_{19}[Fe(CN)_6]_{16}$	$Zn_{10}Ni_6[Fe(CN)_6]_8$	$Zn_{13}Cu_{51}[Fe(CN)_6]_{32}$	■	$Zn_{59}Cd_5[Fe(CN)_6]_{32}$
$Cd_2[Fe(CN)_6]$	–	$Cd_{11}Co_5[Fe(CN)_6]_8$	$Cd_{17}Ni_{15}[Fe(CN)_6]_{16}$	$Cd_9Cu_7[Fe(CN)_6]_8$	$Cd_{45}Zn_{19}[Fe(CN)_6]_{32}$	■

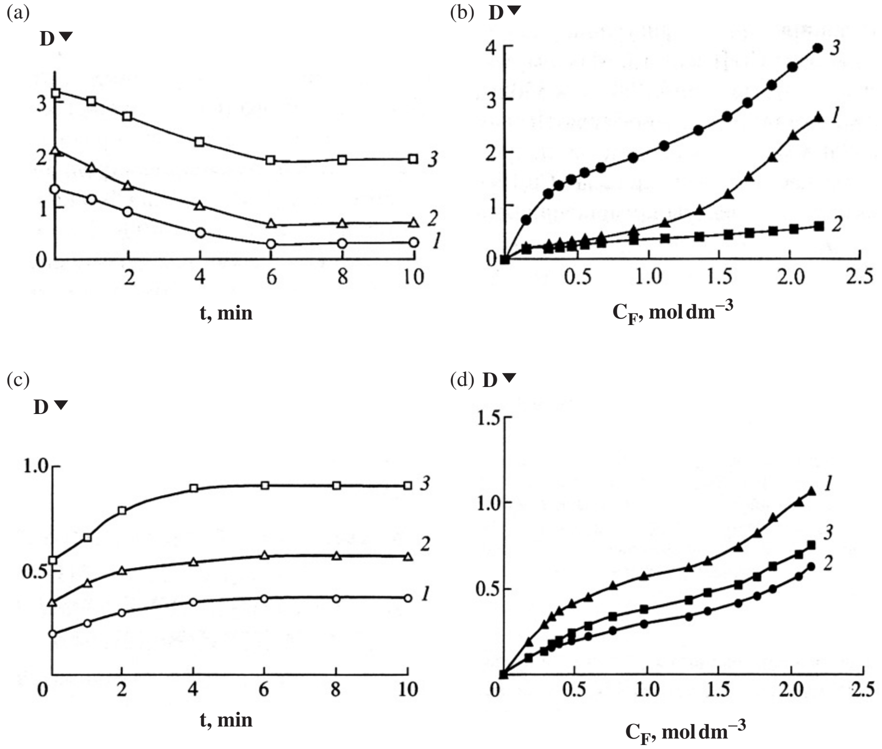


Figure 4. Original $D^{\blacktriangledown} = f(C_F, C^{\circ}_M, t)$ relationships in the $Cu_2[Fe(CN)_6]$–$ZnCl_2$ system (a,b) [94] and in the $Cd_2[Fe(CN)_6]$–$NiCl_2$ system (c,d) [99] in the coordinated section [$C^{\circ}_M = \text{const}$, varied C_F, argument t] (a,c) and in the coordinated section [$C^{\circ}_M = \text{const}$, varied t, argument C_F] (b,d). (a) for $C^{\circ}_M = 7.0 \times 10^{-2}\,\text{mol L}^{-1}$ and $C_F = 0.40$ (1), 1.00 (2) and 1.90 mol dm^{-3} (3); (b) for $C^{\circ}_M = 7.0 \times 10^{-2}\,\text{mol L}^{-1}$ and $t = 6$ min (1), for $Zn_2[Fe(CN)_6]$ (2) and $Cu_2[Fe(CN)_6]$ (3); (c) for $C^{\circ}_M = 7.0 \times 10^{-2}\,\text{mol L}^{-1}$ and $C_F = 0.40$ (1), 1.00 (2) and 1.90 mol dm^{-3} (3); (d) for $C^{\circ}_M = 7.0 \times 10^{-2}\,\text{mol L}^{-1}$ and $t = 6$ min (1), for $Ni_2[Fe(CN)_6]$ (2) and $Cd_2[Fe(CN)_6]$ (3). The optical densities have been measured using a blue filter with a transmission maximum at 450 nm.

Table 2. Heteronuclear(*dd*) metal hexacyanoferrates(II) as a result of electrophilic substitution (ionic exchange) reactions M(II) → Fe(III) in $M_2[Fe(CN)_6]$–$FeCl_3$ systems and Fe(II,III) → M(II) in $Fe_4[Fe(CN)_6]_3$–MCl_2 systems [55, 102].

Electrophilic substitution M(II) → Fe(III)		Electrophilic substitution Fe(II,III) → M(II)	
Mn	$Mn_{19}Fe_{27}[Fe(CN)_6]_{30}$	Mn	–
Co	$Co_{34}Fe_{16}[Fe(CN)_6]_{30}$	Co	$Fe_{26}Co_{18}[Fe(CN)_6]_{30}$
Ni	$Ni_{20}Fe_{25}[Fe(CN)_6]_{30}$	Ni	$Fe_{32}Ni_{28}[Fe(CN)_6]_{30}$
Cu	$Cu_{30}Fe_{18}[Fe(CN)_6]_{30}$	Cu	$Fe_{12}Cu_{40}[Fe(CN)_6]_{30}$
Zn	$Zn_{19}Fe_{25}[Fe(CN)_6]_{30}$	Zn	$Fe_{27}Zn_{19}[Fe(CN)_6]_{30}$
Cd	$Cd_{81}Fe_{26}[Fe(CN)_6]_{60}$	Cd	$Fe_{30}Cd_{11}[Fe(CN)_6]_{30}$

Electrophilic substitution M(II) → Fe(III) takes place for all M indicated above [102, 104], whereas electrophilic substitution Fe(III) → M(II) is observed for all M(II) except Mn(II) [102, 103]. The data indicate that in the $M_2[Fe(CN)_6]$–$FeCl_3$ binary systems studied, $M^{2+} \to Fe^{3+}$ ionic exchange, as well as $Fe^{2+} \to Fe^{3+}$ ionic exchange, occurs. Indeed, with consideration of the law of conservation of charge, compounds $Mn_{19}Fe_{27}[Fe(CN)_6]_{30}$, $Co_{34}Fe_{16}[Fe(CN)_6]_{30}$, $Ni_{20}Fe_{25}[Fe(CN)_6]_{30}$, $Cu_{30}Fe_{18}[Fe(CN)_6]_{30}$, $Zn_{19}Fe_{25}[Fe(CN)_6]_{30}$ and $Cd_{81}Fe_{26}[Fe(CN)_6]_{60}$ [102], must be written as $(Mn^{II})_{19}(Fe^{III})_{28}(Fe^{II})_{29}(CN)_{180}$, $(Co^{II})_{34}(Fe^{III})_{20}(Fe^{II})_{26}(CN)_{180}$, $(Ni^{II})_{20}(Fe^{III})_{30}(Fe^{II})_{25}(CN)_{180}$, $(Cu^{II})_{30}(Fe^{III})_{24}(Fe^{II})_{24}(CN)_{180}$, $(Zn^{II})_{19}(Fe^{III})_{32}(Fe^{II})_{23}(CN)_{180}$ and $(Cd^{II})_{81}(Fe^{III})_{26}(Fe^{II})_{60}(CN)_{360}$, respectively. In practically all these compounds, the number of CN groups and number of Fe^{2+} ions is more than 6.00 indicating that Fe^{3+} substitutes both M^{2+} and Fe^{2+}. The exception is (CdFe)heteronuclear hexacyanoferrate(II) $(Cd^{II})_{81}(Fe^{III})_{26}(Fe^{II})_{60}(CN)_{360}$, where the alignment $n(CN) : n(Fe^{2+})$ is unchanged in comparison to $Cd_2[Fe(CN)_6]$ (6.00) and only $Cd^{2+} \rightarrow Fe^{3+}$ ionic exchange takes place [102].

The formula of $Fe_4[Fe(CN)_6]_3$, in principle, may be written as $(Fe^{III})_4[Fe^{II}(CN)_6]_3$ or $(Fe^{III})(Fe^{II})_3[Fe^{III}(CN)_6]_3$, and, also, as some intermediate between $(Fe^{III})_4[Fe^{II}(CN)_6]_3$ and $(Fe^{III})(Fe^{II})_3[Fe^{III}(CN)_6]_3$, for example $(Fe^{III})_2(Fe^{II})_2[Fe^{III}(CN)_6]_2[Fe^{II}(CN)_6]$. In this connection, it is impossible *a priori* to say whether M^{2+} substitutes *only* Fe^{2+}, *only* Fe^{3+} or M^{2+} substitutes *both* Fe^{2+} and Fe^{3+}. Moreover, it may be asserted that substitution of both iron ions occurs in each $Fe_4[Fe(CN)_6]_3$–MCl_2 system considered (with exception of $Fe_4[Fe(CN)_6]_3$–$MnCl_2$) because after completion of ionic exchange in the solution contacting the $Fe_4[Fe(CN)_6]_3$-matrix, an availability Fe^{2+}, as well as Fe^{3+}, exists [102]. Also, it is impossible to exclude that in the $(Fe^{III})_4[Fe^{II}(CN)_6]_3$–$MCl_2$ systems studied, redox processes take place on a level with ionic exchange. Indeed, compounds having formulas $Fe_{26}Co_{18}[Fe(CN)_6]_{30}$, $Fe_{32}Ni_{28}[Fe(CN)_6]_{30}$, $Fe_{12}Cu_{40}[Fe(CN)_6]_{30}$, $Fe_{27}Zn_{19}[Fe(CN)_6]_{30}$ and $Fe_{30}Cd_{11}[Fe(CN)_6]_{30}$ may be written as $(Fe^{II})_{24}(Fe^{III})_{32}(Co^{II})_{18}(CN)_{180}$, $(Fe^{II})_{62}(Ni^{II})_{28}(CN)_{180}$, $(Fe^{II})_{26}(Fe^{III})_{16}(Cu^{II})_{40}(CN)_{180}$, $(Fe^{II})_{28}(Fe^{III})_{29}(Zn^{II})_{19}(CN)_{180}$ and $(Fe^{II})_{32}(Fe^{III})_{38}(Cd^{II})_{11}(CN)_{180}$, respectively. In conformity with the law of conservation of charge, $(Fe^{III})_4[Fe^{II}(CN)_6]_3$, for example, transformation into $Fe_{32}Ni_{28}[Fe(CN)_6]_{30}$ must be accompanied with *reduction* of initial $(Fe^{III})_4[Fe^{II}(CN)_6]_3$. This reduction can occur either according to equation (13) with acquisition of four electrons per $Fe_4[Fe(CN)_6]_3$ fragment and with substitution only of iron(II), or according to equation (14) with an average of 16 electrons per five $Fe_4[Fe(CN)_6]_3$ fragments and with substitution only of iron(III), or according to equation (15) with substitution of both Fe(II) and Fe(III), because Fe(III) cannot be in the $Fe_{32}Ni_{28}[Fe(CN)_6]_{30}$ composition [55, 102]:

$$10(Fe^{III})_4[Fe^{II}(CN)_6]_3 + 28Ni^{II} + 40e \rightarrow (Fe^{II})_{62}(Ni^{II})_{28}(CN)_{180} + 8Fe^{II} \tag{13}$$

$$10(Fe^{III})_4[Fe^{II}(CN)_6]_3 + 28Ni^{II} + 32e \rightarrow (Fe^{II})_{62}(Ni^{II})_{28}(CN)_{180} + 8Fe^{III} \tag{14}$$

$$10(Fe^{III})_4[Fe^{II}(CN)_6]_3 + 28Ni^{II} + 36e \rightarrow (Fe^{II})_{62}(Ni^{II})_{28}(CN)_{180} + 4Fe^{II} + 4Fe^{III} \tag{15}$$

Transformation of $Fe_4[Fe(CN)_6]_3$ into heteronuclear hexacyanoferrates(II) of cobalt(II), copper(II), zinc(II) and cadmium(II) indicated above, may be formally described by equations (16–19);

$$10(Fe^{III})_4[Fe^{II}(CN)_6]_3 + 18Co^{II} \rightarrow (Fe^{II})_{24}(Fe^{III})_{32}(Co^{II})_{18}(CN)_{180} + 8Fe^{III} + 6Fe^{II} \tag{16}$$

$$10(Fe^{III})_4[Fe^{II}(CN)_6]_3 + 40Cu^{II} \rightarrow (Fe^{II})_{26}(Fe^{III})_{16}(Cu^{II})_{40}(CN)_{180} + 24Fe^{III} + 4Fe^{II} \tag{17}$$

$$10(\mathrm{Fe^{III}})_4[\mathrm{Fe^{II}(CN)_6}]_3 + 19\mathrm{Zn^{II}} \rightarrow (\mathrm{Fe^{II}})_{28}(\mathrm{Fe^{III}})_{29}(\mathrm{Zn^{II}})_{19}(\mathrm{CN})_{180} + 12\mathrm{Fe^{III}} + \mathrm{Fe^{II}} \tag{18}$$

$$10(\mathrm{Fe^{III}})_4[\mathrm{Fe^{II}(CN)_6}]_3 + 11\mathrm{Cd^{II}} \rightarrow (\mathrm{Fe^{II}})_{32}(\mathrm{Fe^{III}})_{38}(\mathrm{Cd^{II}})_{11}(\mathrm{CN})_{180} + 2\mathrm{Fe^{III}} + 8\mathrm{Fe^{II}} \tag{19}$$

it is impossible to exclude possibility of redox processes in any of these cases, for example equation (20):

$$\begin{aligned}10(\mathrm{Fe^{III}})_4[\mathrm{Fe^{II}(CN)_6}]_3 + 18\mathrm{Co^{II}} - 4e \rightarrow (\mathrm{Fe^{II}})_{24}(\mathrm{Fe^{III}})_{32}(\mathrm{Co^{II}})_{18}(\mathrm{CN})_{180}\\ + 12\mathrm{Fe^{III}} + 2\mathrm{Fe^{II}}\end{aligned} \tag{20}$$

As in the case of **$\{M_2[Fe(CN)_6]\}$**– $M'Cl_2$ systems, formation of any compound indicated in table 2, occurs *only in the gelation-immobilized matrix*, not by interaction of $M_2[Fe(CN)_6]$ with $FeCl_3$ and $Fe_4[Fe(CN)_6]_3$ with MCl_2 in solution or in solid phase, indicating a specific role of gelatin-immobilized matrix in electrophilic substitution. It is obvious additional investigations are necessary here.

One can assume that such reactions may also proceed with the participation of separate, especially stable and kinetically inert, cationic complexes (for instance, complexes of the *d*-elements with 2,2′-dipyridyl and 1,10-phenanthroline); the indicated ligands remain in the inner sphere of the formed coordination compounds after the reaction ends [55]. However, this assumption requires substantiation.

3.3. *Nucleophilic substitution in the metal hexacyanoferrate(II) gelatin-immobilized matrices*

Nucleophilic substitution may be written as equations (21) for $M_2[Fe(CN)_6]$, (22) for $M_4[Fe(CN)_6]_3$ and (23) for $M[Fe(CN)_6]$ (m, n, r, s– whole numbers) [55]:

$$m\mathrm{M_2[Fe(CN)_6]} + 2n\mathrm{H_kL} \rightarrow 2[\mathrm{M_m(H_{k-r}L)_n}]^{(2m-nr)+} + 2nr\mathrm{H^+} + m[\mathrm{Fe(CN)_6}]^{4-} \tag{21}$$

$$m\mathrm{M_4[Fe(CN)_6]_3} + 4n\mathrm{H_kL} \rightarrow 4[\mathrm{M_m(H_{k-r}L)_n}]^{(3m-nr)+} + 4nr\mathrm{H^+} + 3m[\mathrm{Fe(CN)_6}]^{4-} \tag{22}$$

$$m\mathrm{M[Fe(CN)_6]} + 2n\mathrm{H_kL} \rightarrow 2[\mathrm{M_m(H_{k-r}L)_n}]^{(2m-nr)+} + 2nr\mathrm{H^+} + m[\mathrm{Fe(CN)_6}]^{4-} \tag{23}$$

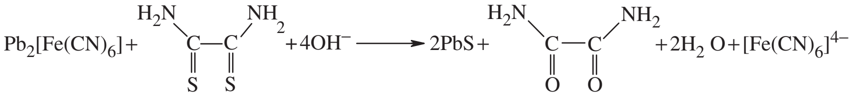
One expects that attack on the Fe–CN–M groups contained in any metal hexacyanoferrate(II) coordination polymer their behavior will be determined by the ratio of the energies of the metal-nitrogen bond (E_{M-N}) and the metal-oxygen bond (E_{M-O}). If $E_{M-N} > E_{M-O}$, then metal hexacyanoferrate(II) will be stable to action of the OH^- in solutions in contact with the metal hexacyanoferrate(II) matrix. If $E_{M-N} < E_{M-O}$, then the M–N bond will be replaced by M–O bonds; i.e. the destruction of the starting metal hexacyanoferrate(II) takes place under the action of OH^- with formation of polymer oxohydroxides of the given metal ion [60–62]. The first situation is observed for complexation in the metal hexacyanoferrate(II) matrix, for Co(III) and Ni(II), while the second is observed for M = Fe(III), Co(II), Cu(II), UO_2(VI). Indeed, all of the binary systems studied so far fall into one of these types. In the first, complexation follows the formal S_N2 mechanism [60, 61, 106–122], while in the second complexation follows the formal pseudo-S_N1 mechanism [60–62, 105, 123–147]. The key factor is the nature of the metal hexacyanoferrate(II) [55, 60]. In the systems of the first type, both homo- and heteroligand (containing molecules of the corresponding ligand with some deprotonation and the $[Fe(CN)_6]^{4-}$ anion) chelate coordination compounds can form. The second type systems only form homoligand complexes (although, theoretically, one can expect coordination compounds with the OH^- group in the inner sphere in addition to the chelate ligand).

Every reported metal hexacyanoferrate(II) matrix displays only one variant of complexation when, depending on the nature of the metal ion (but independent of the ligand nature), the heteroligand complexes are formed either at all times (as with the $KCo[Fe(CN)_6]$-matrix) or, conversely, never [55, 60]. The only exception here is $Ni_2[Fe(CN)_6]$-matrix, where the ligand nature determines which of the variants is to be realized (the first variant, in the case of the N,S-donor ligands capable of producing at least two forms with different extents of deprotonation (H_2L) and the second variant, for N,S-donor ligands that can form at $pH > 7$ only one such form (HL)), as well as for N,O-donor ligands. There is no doubt that, of the investigated systems, the Ni(II)-dithiooxamide system [60, 61, 106–109] is of special interest. Analysis of the $D^{\blacktriangledown} = f(C_F, C_L^{\circ}, t)$ curves for this system reveals a stepwise elimination of $[Fe(CN)_6]^{4-}$ from the inner sphere of the $Ni_2[Fe(CN)_6]$ coordination polymer that follows the S_N2 mechanism with an increasing concentration of the ligand in the immobilized matrix and subsequent formation of the ligand-deficient complex of composition $(Ni_2L)_2[Fe(CN)_6]$ and monomeric and polymeric proton-deficient chelate complexes with the ratio of the metal ion: a double deprotonated ligand equal to 1 : 1, insoluble in water, and a soluble 1 : 2 complex with singly and doubly deprotonated ligands in the inner sphere. In this case, at $pH < 5$, the 1 : 1 monomer chelate complex easily and irreversibly transforms into the 1 : 2 polymer with a singly-deprotonated ligand. The processes of formation of the indicated complexes in the $Ni_2[Fe(CN)_6]$–gelatin-immobilized matrix have been described [106–109, 112].

Two types of attack on the $Ni_2[Fe(CN)_6]$ coordination polymer are possible by a bidentate ligand such as dithiooxamide [108, 109, 112], either on one vacant coordination position or on two such positions belonging to different atoms of the given *d*-element. The latter type, which should theoretically result in the formation of the ligand-deficient complex, may only be observed when the reaction volume is strongly restricted and the molecules of the entering ligand are deficient in number. Both of these factors can be simultaneously observed in complexing in the immobilized matrix, but this is not the case with a solution or a solid phase. The formation of the ligand-deficient complex in this system should be facilitated by availability of two donor centers (atoms of sulfur) in dithiooxamide, through which σ-donor and π-acceptor interactions simultaneously occur between Ni(II) and the given ligands leading to formation of quite strong bonds [108, 112]. In addition, because of the exceedingly small reaction volume of the matrix, the concentration of OH^- becomes very high, which causes attack by these ions on the axial positions in the Ni(II) chelate complex of 1 : 2 composition following the Langford–Gray mechanism, the substitution of one ligand by two OH groups, and, then, the formation of the monomeric proton-deficient chelate complex $[NiL(OH_2)_2]$ [109]. At a sufficiently high concentration of this complex in the matrix, its molecules can aggregate to give a coordination polymer which is promoted by the restricted reaction volume [108, 109, 112]. Thus, in the complexing of Ni(II) with dithiooxamide in the $Ni_2[Fe(CN)_6]$ matrix, at least five different coordination compounds can be synthesized, whereas in solution [107–109] only the

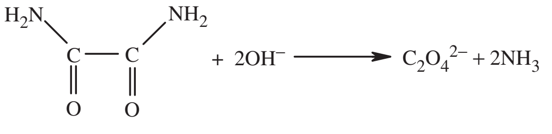
1 : 2 insoluble chelate complex is formed. This is clear evidence of high synthetic potential for complexation in matrices [110–114, 116, 118].

Complexation in the Ni(II) hexacyanoferrate(II) matrix yields ligand-deficient, proton-deficient, and polymer complexes. Complexation in the Cu(II) hexacyanoferrate(II) matrix [62, 113–135] confirms the assumption about formation of dimers and polymers (observed, in particular, in the Cu(II)-quinoxaline-2,3-dithiol [62, 124]). Complexation in the Co(III) hexacyanoferrate(II) matrix [116–121] gives intermediate coordination compounds that were not isolated from solutions. The details of nucleophilic substitution in the metal hexacyanoferrate(II) matrices in the specific 3*d*-metal ion-ligand systems have been discussed [55, 57]. The possibility of complexation in *f*-metal hexacyanoferrate(II) gelatin-immobilized matrices, i.e., in $(UO_2)_2[Fe(CN)_6]$ matrix, was shown with participation of certain 8-hydroxy- and 8-mercaptoquinolines [144–147]. The data indicate that the interaction of the dioxouranyl(VI) ion with the respective ligand is preceded by destruction of $(UO_2)_2[Fe(CN)_6]$ under action of OH^-; however, these data are not sufficient to make more substantiated conclusions. Examples of $D^{\blacktriangledown} = f(C_F, C_L^{\circ}, t)$ relationships are presented in figure 5. A full list of complexation processes discovered in the various metal hexacyanoferrate(II) gelatin-immobilized matrix systems is presented in table 3. Complexation with participation of *p*-metal hexacyanoferrate(II) gelatin-immobilized matrices is related to the Pb(II)-dithiooxamide system [148, 149]. As distinct from *d*-metal hexacyanoferrate(II) gelatin-immobilized matrix systems discussed above, the final product of complexation in the Pb(II)-dithiooxamide system is not Pb(II) complex with the ligand, but lead(II) sulphide PbS forming according to equation (24):



$$Pb_2[Fe(CN)_6] + H_2NC(=S)C(=S)NH_2 + 4OH^- \longrightarrow 2PbS + H_2NC(=O)C(=O)NH_2 + 2H_2O + [Fe(CN)_6]^{4-} \quad (24)$$

In the solution contacting the $Pb_2[Fe(CN)_6]$-matrix, after completion of complexation, oxalate and ammonia which result from alkaline destruction of oxamide $H_2NC(=O)C(=O)NH_2$ (equation (25)) are observed:



$$H_2NC(=O)C(=O)NH_2 + 2OH^- \longrightarrow C_2O_4^{2-} + 2NH_3 \quad (25)$$

The processes of complex formation should also occur in the other *d*- and *f*-metal hexacyanoferrate(II) matrices, but they have not yet been realized. It also becomes obvious that the number of nucleophilic substitution reactions can increase; in particular, one may expect that similar processes in metal hexacyanoferrate(II) gelatin-immobilized matrices may occur when they come into contact not only with the liquid-phase, but also with gas-phase systems containing (for example) CO, NO, NH_3, and PF_3. Apparently, complexation processes with various (N, O, S)–ligands may proceed as well in many other *d*- and *f*-metal hexacyanoferrate(II) gelatin-immobilized matrix systems, but publications have not appeared [55].

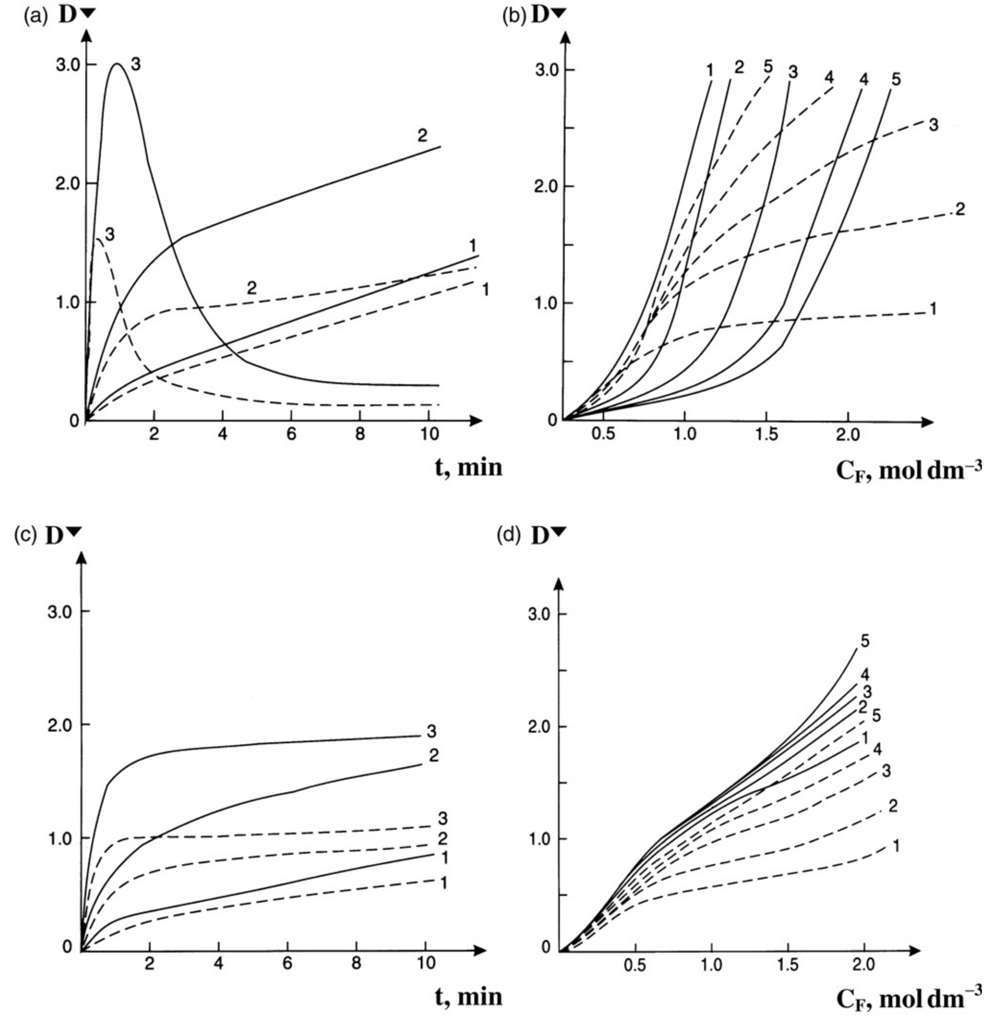


Figure 5. Original $D^{\blacktriangledown} = f(C_F, C^{\circ}_L, t)$ relationships in the $Ni_2[Fe(CN)_6]$-dithiooxamide system (a, b) and in the $Ni_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol system (c, d) [108] in the coordinated section [$C_F = \text{const}$, varied C°_L, argument t] (a, c) and in the coordinated section [$C^{\circ}_L = \text{const}$, varied t, argument C_F] (b, d). (a) at $C_F = 0.57\,\text{mol dm}^{-3}$ (- - - - -) and $0.92\,\text{mol dm}^{-3}$ (——) for $C^{\circ}_L = 1.0 \times 10^{-3}\,\text{mol L}^{-1}$ (1), $4.0 \times 10^{-3}\,\text{mol L}^{-1}$ (2) and $3.5 \times 10^{-2}\,\text{mol L}^{-1}$ (3); (b) at $C^{\circ}_L = 4.0 \times 10^{-3}\,\text{mol L}^{-1}$ (- - - - -) and $3.5 \times 10^{-2}\,\text{mol L}^{-1}$ (——) and $t = 1$ min (1), 2 min (2), 4 min (3), 6 min (4), 10 min (5); (c) at $C_F = 0.75\,\text{mol dm}^{-3}$ (- - - - -) and $1.20\,\text{mol dm}^{-3}$ (——) for $C^{\circ}_L = 2.0 \times 10^{-3}\,\text{mol L}^{-1}$ (1), $6.0 \times 10^{-3}\,\text{mol L}^{-1}$ (2) and $2.0 \times 10^{-2}\,\text{mol L}^{-1}$ (3); (d) at $C^{\circ}_L = 6.0 \times 10^{-3}\,\text{mol L}^{-1}$ (- - - - -) and $2.0 \times 10^{-2}\,\text{mol L}^{-1}$ (——) and $t = 1$ min (1), 2 min (2), 4 min (3), 6 min (4), 10 min (5). The optical densities have been measured using a blue filter with a transmission maximum at 450 nm.

3.4. *Soft template synthesis in the metal hexacyanoferrate(II) gelatin-immobilized matrices*

Among chelate complexation reactions of special interest are those in which the polydentate ligands form as a result of coupling of two or more simpler organic compounds in the presence of a specific metal ion; in this case, at least one acts as

Table 3. Nucleophilic substitution reactions in metal hexacyanoferrate(II) gelatin-immobilized matrices upon contact with aqueous solutions of various N–, O–, S–, P–containing chelate ligands.

	Process parameters				
Ligands and nucleophilic substitution reactions	C_F, mol dm^{-3}	C_L^0, mol dm^{-3}	*t* (min)	pH	Ref.
1	2	3	4	5	6
Binary systems containing $KFe[Fe(CN)_6]$-gelatin-immobilized matrix materials					
8-Hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 7-methyl-8-hydroxyquinoline (HL)					105, 139, 143
$KFe[Fe(CN)_6] + 2OH^- \rightarrow Fe(OH)_2 + [Fe(CN)_6]^{3-} + K^+$	0.1–2.0	5.0×10^{-6}–1.0×10^{-4}	4–10	11–13	
$KFe[Fe(CN)_6] + 3OH^- \rightarrow FeO(OH) + [Fe(CN)_6]^{4-} + K^+$	0.1–2.0	5.0×10^{-6}–1.0×10^{-4}	4–10	11–13	
$Fe(OH)_2 + 2HL \rightarrow FeL_2 + 2H_2O$	0.1–2.0	5.0×10^{-3}–2.0×10^{-2}	6–10	11–13	
$4FeL_2 + O_2 + 4HL \rightarrow 4FeL_3 + 2H_2O$	0.1–0.5	1.0×10^{-1}–2.0×10^{-1}	6–10	11–13	
1-Nitrozo-2-naphthol and 2-nitrozo-1-naphthol and isonitrozoacetone (HL)					55
$KFe[Fe(CN)_6] + 2OH^- \rightarrow Fe(OH)_2 + [Fe(CN)_6]^{3-} + K^+$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–13	
$KFe[Fe(CN)_6] + 3OH^- \rightarrow FeO(OH) + [Fe(CN)_6]^{4-} + K^+$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–13	
$Fe(OH)_2 + 2HL \rightarrow FeL_2 + 2H_2O$	0.1–2.0	5.0×10^{-3}–6.0×10^{-2}	4–10	11–13	
8-Mercaptoquinoline, 5-chloro-8-mercaptoquinoline, 5-bromo-8-mercaptoquinoline and 5-thiomethyl-8-mercaptoquinoline (HL)					140–142
$KFe[Fe(CN)_6] + 2OH^- \rightarrow Fe(OH)_2 + [Fe(CN)_6]^{3-} + K^+$	0.1–2.0	1.0×10^{-6}–5.0×10^{-5}	4–10	11–13	
$KFe[Fe(CN)_6] + 3OH^- \rightarrow FeO(OH) + [Fe(CN)_6]^{4-} + K^+$	0.1–2.0	1.0×10^{-6}–5.0×10^{-5}	4–10	11–13	
$4Fe(OH)_2 + 12HL + O_2 \rightarrow 4FeL_3 + 10H_2O$	0.1–2.0	1.0×10^{-2}–3.0×10^{-2}	4–10	11–13	
Binary systems containing $Co_2[Fe(CN)_6]$-gelatin-immobilized matrix materials					
1-Nitrozo-2-naphthol and 2-nitrozo-1-naphthol (HL)					55, 136, 137
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-5}	6–10	12–14	
$Co_2[Fe(CN)_6] + 4HL + 4OH^- \rightarrow 2CoL_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–1.0	5.0×10^{-3}–2.0×10^{-2}	2–10	12–13	
$4CoL_2 + O_2 + 4HL \rightarrow 4CoL_3 + 2H_2O$	0.1–0.2	1.5×10^{-2}–3.0×10^{-2}	>10	12–13	
$2CoL_2 + 2H^+ + 6H_2O \rightarrow {}_3 + CoL_3 + [Co(H_2O)_6]^{2+} + H_2L$			6–10	2–3	
Dithiooxamide (H_2L)					55
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-5}	6–10	12–14	
$4Co(OH)_2 + 12H_2L + O_2 \rightarrow 4Co(HL)_3 + 10H_2O$	0.1–0.7	1.0×10^{-2}–1.0×10^{-1}	4–10	11–13	
N,*N*′-diphenylthiooxamide and *N*,*N*′-diphenyldithiooxamide (H_2L)					55
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-5}	6–10	12–14	
$4Co(OH)_2 + 12H_2L + O_2 \rightarrow 4Co(HL)_3 + 10H_2O$	0.1–0.7	1.5×10^{-2}–1.0×10^{-1}	4–10	11–13	

(*Continued*)

Table 3. Continued.

Ligands and nucleophilic substitution reactions	Process parameters				Ref.
	C_F, mol dm^{-3}	C_L^0, mol dm^{-3}	t (min)	pH	
1	2	3	4	5	6
Quinoxaline-2,3-dithiol (H_2L)					55
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-5}	6–10	12–14	
$4Co(OH)_2 + 12H_2L + O_2 + 6OH^- \rightarrow 2Co_2L_3 + 6HL^- + 16H_2O$	0.1–0.5	5.0×10^{-2}–1.0×10^{-1}	6–10	11–13	
8-Mercaptoquinoline (HL)					55, 138
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-5}	6–10	12–14	
$4Co(OH)_2 + 12HL + O_2 \rightarrow 4CoL_3 + 10H_2O$	0.1–0.7	1.0×10^{-2}–5.0×10^{-2}	4–10	11–13	
5-Chloro-8-mercaptoquinoline and 5-thiome-thyl-8-mercaptoquinoline (HL)					55, 138
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-5}	6–10	12–14	
$4Co(OH)_2 + 12HL + O_2 \rightarrow 4CoL_3 + 10H_2O$	0.1–0.7	1.0×10^{-2}–5.0×10^{-2}	4–10	11–13	
N-diisopropoxythiophosphoryl-thiobenzamide (HL)					117, 133
$Co_2[Fe(CN)_6] + 4OH^- \rightarrow 2Co(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–1.0	1.0×10^{-6}–1.0×10^{-4}	4–10	10–12	
$2Co(OH)_2 + HL \rightarrow [CoL(OH)(OH_2)]$	0.2–1.0	1.0×10^{-3}–1.0×10^{-1}	1–6	10–12	
$[CoL(OH)(OH_2)] + HL \rightarrow CoL_2 + 2H_2O$	0.1–0.8	5.0×10^{-2}–1.0×10^{-1}	6–10	10–12	
Binary systems containing $Cu_2[Fe(CN)_6]$-gelatin-immobilized matrix materials					
8-Hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 7-methyl-8-hydroxyquinoline (HL)					55
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$Cu(OH)_2 + 2HL \rightarrow CuL_2 + 2H_2O$	0.1–1.5	1.0×10^{-2}–2.0×10^{-1}	4–10	11–13	
α-Benzoinoxime (H_2L)					55
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–13	
$nCu(OH)_2 + nH_2L \rightarrow (CuL)_n + 2nH_2O$	0.1–1.5	1.0×10^{-2}–3.0×10^{-2}	6–10	11–13	
Dithiooxamide (H_2L)					55, 60, 109, 123, 128
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$nCu(OH)_2 + nHL^- + nH_2O \rightarrow [CuL(OH_2)_2]_n + nOH^-$	0.4–1.5	5.0×10^{-4}–5.0×10^{-3}	1–6	11–13	
$nCu(OH)_2 + 2nHL^- \rightarrow [Cu(HL)_2]_n + 2nOH^-$	0.1–1.0	1.0×10^{-2}–3.0×10^{-2}	2–10	11–13	
$[Cu(HL)_2]_n + nHL^- \rightarrow n[Cu(HL)_2(HL)]^-$	0.1–0.5	1.0×10^{-1}–3.0×10^{-1}	4–10	11–13	
N,*N*′-Diphenylthiooxamide and *N*,*N*′-Diphenyldithiooxamide (H_2L)					55, 128
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$Cu(OH)_2 + 2H_2L \rightarrow Cu(HL)_2 + 2H_2O$	0.1–1.5	2.0×10^{-2}–5.0×10^{-2}	1–10	11–13	

Quinoxaline-2,3-dithiol (H_2L)					62, 124, 128
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$2Cu(OH)_2 + 2H_2L \rightarrow Cu_2L_2\ (OH_2)_4$	0.3–2.0	2.0×10^{-3}–2.0×10^{-1}	4–10	11–14	
$Cu(OH)_2 + 2H_2L \rightarrow Cu(HL)_2 + 4H_2O$	0.1–2.0	1.0×10^{-2}–2.0×10^{-2}	2–10	11–13	
$Cu(HL)_2 + HL^- \rightarrow [Cu(HL)_2(HL)]^-$	0.1–0.5	3.0×10^{-2}–2.0×10^{-1}	4–10	11–13	
1,2-Dithiocarbamylhydrazine, (1-carbamyl-2-thiocarbamyl)hydrazine (H_2L)					55, 62, 127, 134
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$2Cu(OH)_2 + 2H_2L \rightarrow Cu_2L_2\ (OH_2)_2 + 2H_2O$	0.1–1.5	3.0×10^{-3}–5.0×10^{-2}	2–10	10–13	
$Cu_2L_2\ (OH_2)_2 + 2HL^- \rightarrow 2[CuLHL]^- + 2H_2O$	0.1–0.3	1.0×10^{-1}–5.0×10^{-1}	4–10	11–13	
8-Mercaptoquinoline, 5-chloro-8-mercaptoquinoline (HL)					55, 57, 129, 135
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$2Cu(OH)_2 + 2HL \rightarrow CuL_2 + 2H_2O$	0.1–2.0	1.0×10^{-2}–3.0×10^{-2}	4–10	11–13	
5-Thiomethyl-8-mercaptoquinoline, 5-bromo-8-mercaptoquinoline (HL)					135
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$2Cu(OH)_2 + 2HL \rightarrow CuL_2 + 2H_2O$	0.1–1.5	1.0×10^{-2}–3.0×10^{-2}	4–10	11–13	
$nCuL_2 \rightarrow [CuL_2]_n$	1.5–2.0	2.0×10^{-2}–5.0×10^{-2}	4–10	11–13	
5,8-Dimercaptoquinoline (H_2L)					135
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$2nCu(OH)_2 + 2nH_2L \rightarrow [Cu_2L_2(H_2O)_2]_n$	0.1–1.5	1.0×10^{-2}–3.0×10^{-2}	4–10	11–13	
$[Cu_2L_2(H_2O)_2]_n + nH_2L \rightarrow 2nCu(HL)_2 + 2nH_2O$	1.5–2.0	2.0×10^{-2}–5.0×10^{-2}	4–10	11–13	
1-Methyl-1-phenyl-3-benzoylthiourea, 1,1-dibenzyl-3-benzoylthiourea (HL)					125, 126, 131
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	12–14	
$2Cu(OH)_2 + HL \rightarrow [CuL(OH)(OH_2)]$	0.2–2.0	1.0×10^{-2}–5.0×10^{-2}	1–4	12–14	
$[CuL(OH)(OH_2)] + HL \rightarrow CuL_2 + 2H_2O$	0.1–1.0	1.0×10^{-2}–5.0×10^{-2}	4–10	12–14	
1-*N*-pentamethylene-3-benzoylthiourea, 1-*N*-3-oxatetramethylene-3-benzoylthiourea (HL)					125, 131
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	12–14	
$2Cu(OH)_2 + HL \rightarrow [CuL(OH)(OH_2)]$	0.2–2.0	1.0×10^{-2}–5.0×10^{-2}	1–4	12–14	
$[CuL(OH)(OH_2)] + HL \rightarrow CuL_2 + 2H_2O$	0.1–1.0	1.5×10^{-2}–5.0×10^{-2}	4–10	12–14	
1-(2-hydroxy)phenyl-3-benzoylthiourea (H_2L)					131
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	11–14	
$Cu(OH)_2 + H_2L \rightarrow [CuHL(OH)(OH_2)]$	0.1–0.7	1.5×10^{-3}–2.5×10^{-2}	1–10	11–14	
$[CuHL(OH)(OH_2)] + H_2L + Cu(OH)_2 \rightarrow Cu_2L_2 + 2H_2O$	0.7–2.0	1.5×10^{-2}–2.5×10^{-2}	1–10	11–14	
$[CuHL(OH)(OH_2)] + H_2L \rightarrow Cu(HL)_2 + 2H_2O$	0.1–2.0	3.0×10^{-2}–5.0×10^{-2}	1–10	11–14	

(*Continued*)

Table 3. Continued.

Ligands and nucleophilic substitution reactions	Process parameters				Ref.
	C_F, mol dm^{-3}	C_L^0, mol dm^{-3}	*t* (min)	pH	
1	2	3	4	5	6
N-diisopropoxythiophosphoryl-thiobenzamide (HL)					117, 133
$Cu_2[Fe(CN)_6] + 4OH^- \rightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-4}	4–10	10–12	
$2Cu(OH)_2 + HL \rightarrow [CuL(OH)(OH_2)]$	0.2–2.0	1.0×10^{-2}–1.0×10^{-1}	1–4	10–12	
$[CuL(OH)(OH_2)] + HL \rightarrow CuL_2 + 2H_2O$	0.1–1.0	1.0×10^{-2}–1.0×10^{-1}	4–10	10–12	
Binary systems containing $KCo[Fe(CN)_6]$*-gelatin-immobilized matrix materials*					
Dithiooxamide (H_2L)					118, 120
$KCo[Fe(CN)_6] + H_2L + OH^- \rightarrow [Co(HL)]_4[Fe(CN)_6]_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	3.0×10^{-3}–5.0×10^{-3}	1–4	11–13	
$[Co(HL)]_4[Fe(CN)_6]_2 + 4H_2L + 4OH^- \rightarrow [Co(HL)_2]_4[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	5.0×10^{-3}–1.0×10^{-2}	1–4	11–13	
$[Co(HL)_2]_4[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow [Co(HL)_3] + [Fe(CN)_6]^{4-} + 4H_2O$	0.3–1.2	3.0×10^{-2}–5.0×10^{-2}	2–10	11–13	
$[Co(HL)_3] + H_2L + OH^- \rightarrow [Co(HL)_2(HL)_2]^- + H_2O$	0.3–0.7	3.0×10^{-2}–2.0×10^{-1}	4–10	11–13	
N,N′-diphenylthiooxamide (H_2L)					120
$4KCo[Fe(CN)_6] + 2H_2L + 2OH^- \rightarrow 2[Co_2L][Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O + 2K^+$	0.1–2.0	1.0×10^{-3}–3.0×10^{-3}	<1	11–13	
$KCo[Fe(CN)_6] + H_2L + OH^- \rightarrow [Co(HL)]_4[Fe(CN)_6]_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.0×10^{-3}–3.0×10^{-3}	2–6	11–13	
$[Co(HL)]_4[Fe(CN)_6]_2 + 4H_2L + 4OH^- \rightarrow [Co(HL)_2]_4[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	4.0×10^{-3}–2.0×10^{-2}	2–10	11–13	
$[Co(HL)_2]_4[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow [Co(HL)_3] + [Fe(CN)_6]^{4-} + 4H_2O$	0.2–1.0	2.0×10^{-2}–5.0×10^{-2}	2–10	11–13	
N,N′-diphenyldithiooxamide (H_2L)					121
$KCo[Fe(CN)_6] + H_2L + OH^- \rightarrow [Co(HL)]_4[Fe(CN)_6]_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.0×10^{-3}–4.0×10^{-3}	<1	11–13	
$[Co(HL)]_4[Fe(CN)_6]_2 + 4H_2L + 4OH^- \rightarrow [Co(HL)_2]_4[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.0×10^{-2}–2.0×10^{-2}	1–4	11–13	
$[Co(HL)_2]_4[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow [Co(HL)_3] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–0.8	3.0×10^{-2}–4.0×10^{-2}	2–10	11–13	
8-mercaptoquinoline, 5-chloro-8-mercaptoquinoline, 5-bromo-8-mercaptoquinoline (HL)					60, 119, 122
$KCo[Fe(CN)_6] + HL + OH^- \rightarrow [CoL]_4[Fe(CN)_6]_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	6.0×10^{-3}–1.5×10^{-3}	1–6	11–13	
$[CoL]_4[Fe(CN)_6]_2 + 4HL + 4OH^- \rightarrow [CoL_2]_4[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.5×10^{-2}–3.0×10^{-2}	2–6	11–13	
$[CoL_2]_4[Fe(CN)_6] + 4HL + 4OH^- \rightarrow [CoL_3] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–0.8	3.0×10^{-2}–5.0×10^{-2}	6–10	11–13	
Binary systems containing $Ni_2[Fe(CN)_6]$*-gelatin-immobilized matrix materials*					
Dimethylglyoxime (H_2L)					55, 60
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.0×10^{-2}–5.0×10^{-1}	1–10	9–12	
$Ni(HL)_2 + OH^- + H_2O \rightarrow NiL(OH)_2 + HL^-$	0.1–2.0	1.0×10^{-2}–5.0×10^{-1}	1–10	13–14	
$Ni(HL)_2 + 2H^+ + 2Cl^- \rightarrow [Ni(H_2L)_2]Cl_2$	0.1–2.0	1.0×10^{-2}–5.0×10^{-1}	1–10	2–4	
$[Ni(H_2L)_2]Cl_2 \rightarrow [Ni(H_2L)Cl_2] + H_2L$	0.1–2.0	1.0×10^{-2}–5.0×10^{-1}	1–10	2–4	

α-Benzyldioxime (H_2L)					55
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	3.0×10^{-3}–8.0×10^{-2}	1–10	10–13	
$Ni(HL)_2 + 2H^+ + 2Cl^- \rightarrow [Ni(H_2L)_2]Cl_2$	0.1–2.0	5.0×10^{-3}–1.5×10^{-1}	1–10	2–4	
Nioxime (H_2L)					55
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	3.0×10^{-3}–8.0×10^{-2}	1–10	10–13	
$Ni(HL)_2 + 2H^+ + 2Cl^- \rightarrow [Ni(H_2L)_2]Cl_2$	0.1–2.0	6.0×10^{-3}–2.0×10^{-1}	1–10	2–4	
Dithiooxamide (H_2L)					55, 60, 61, 106–109
$2Ni_2[Fe(CN)_6] + 2H_2L + 4OH^- \rightarrow (Ni_2L)_2[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.0×10^{-4}–1.0×10^{-3}	<1	11–13	
$Ni_2[Fe(CN)_6] + 2H_2L + 4OH^- \rightarrow 2NiL(OH_2)_2 + [Fe(CN)_6]^{4-}$	0.3–2.0	2.0×10^{-3}–2.0×10^{-2}	1–10	11–13	
$nNiL(OH_2)_2 \rightarrow [NiL(OH_2)_2]_n$	1.0–2.0	2.0×10^{-2}–5.0×10^{-2}	2–10	11–13	
$2nNiL(OH_2)_2 + 2nH^+ \rightarrow [Ni(HL)_2]_n + nNi^{2+} + 4nH_2O$	–	–	<1	2–5	
$NiL(OH_2)_2 + H_2L + OH^- \rightarrow [NiLHL]^- + 3H_2O$	0.1–1.0	1.0×10^{-1}–2.5×10^{-1}	4–10	11–13	
N,*N*′-Diphenyldithiooxamide (H_2L)					108, 113
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	1.0×10^{-3}–3.0×10^{-2}	4–10	12–14	
N,*N*′-Diphenylthiooxamide (H_2L)					55, 113, 116
$2Ni_2[Fe(CN)_6] + 2H_2L + 4OH^- \rightarrow (Ni_2L)_2[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	0.2–2.0	2.0×10^{-4}–2.0×10^{-3}	1–10	12–14	
$Ni_2[Fe(CN)_6] + 2H_2L + 4OH^- \rightarrow 2NiL(OH_2)_2 + [Fe(CN)_6]^{4-}$	0.1–1.5	1.0×10^{-3}–3.0×10^{-2}	1–10	11–13	
$2NiL(OH_2)_2 + 2H^+ \rightarrow Ni(HL)_2 + Ni^{2+} + 4H_2O$	–	–	<1	3–5	
$Ni(HL)_2 + H_2O + OH^- \rightarrow NiL(OH_2)_2 + 3H_2O$	–	–	<1	10–13	
$NiL(OH_2)_2 + H_2L + OH^- \rightarrow [NiLHL]^- + 3H_2O$	0.1–0.5	1.0×10^{-3}–3.0×10^{-2}	6–10	11–13	
Quinoxaline-2,3-dithiol (H_2L)					60, 61, 108, 111, 112
$2Ni_2[Fe(CN)_6] + 2H_2L + 4OH^- \rightarrow (Ni_2L)_2[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O$	1.5–2.0	1.0×10^{-4}–2.0×10^{-3}	1–4	11–13	
$Ni_2[Fe(CN)_6] + 2H_2L + 4OH^- \rightarrow 2NiL(OH_2)_2 + [Fe(CN)_6]^{4-}$	0.2–1.0	5.0×10^{-3}–1.0×10^{-1}	1–10	11–13	
$2NiL(OH_2)_2 + 2H^+ \rightarrow Ni(HL)_2 + Ni^{2+} + 4H_2O$	–	–	<1	2–5	
$Ni(HL)_2 + H_2O + OH^- \rightarrow NiL(OH_2)_2 + 3H_2O$	–	–	<1	9–13	
8-Mercaptoquinoline, 5-thiomethyl-8-mercaptoquinoline (HL)					55, 114, 115
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	2.0×10^{-3}–3.0×10^{-2}	4–10	10–13	
5-Chloro-8-mercaptoquinoline, 5-bromo-8-mercaptoquinoline (HL)					55, 115
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	2.0×10^{-3}–4.0×10^{-2}	4–10	10–13	
5,8-Dimercaptoquinoline (H_2L)					55, 114, 115
$Ni_2[Fe(CN)_6] + 4H_2L + 4OH^- \rightarrow 2Ni(HL)_2 + [Fe(CN)_6]^{4-} + 4H_2O$	0.1–2.0	2.0×10^{-3}–3.0×10^{-2}	4–10	10–13	
$Ni_2[Fe(CN)_6] + 2H_2L + 2OH^- \rightarrow Ni_2L_2\ (OH_2)_2 + [Fe(CN)_6]^{4-} + 2H^+$	1.0–2.0	1.0×10^{-3}–5.0×10^{-3}	1–4	11–13	

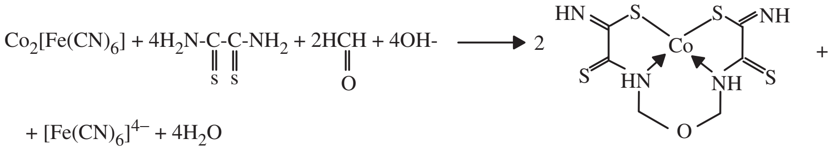
(Continued)

Table 3. Continued.

Ligands and nucleophilic substitution reactions	Process parameters				Ref.
	C_F, mol dm^{-3}	C_L^0, mol dm^{-3}	*t* (min)	pH	
1	2	3	4	5	6
N-diisopropoxythiophosphoryl-thiobenzamide (HL)					117
$2Ni_2[Fe(CN)_6] + 2HL + 2OH^- \rightarrow [Ni_2LOH]_2[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 2H^+$	1.5–2.0	1.0×10^{-3}–5.0×10^{-3}	1–4	10–12	
$Ni_2[Fe(CN)_6] + 2HL + 4OH^- \rightarrow 2NiL(OH)(OH_2) + [Fe(CN)_6]^{4-}$	1.0–1.2	2.0×10^{-3}–1.0×10^{-2}	4–6	10–12	
$Ni_2[Fe(CN)_6] + 4HL + 4OH^- \rightarrow 2NiL_2 + [Fe(CN)_6]^{4-}$	0.1–0.8	$>5.0 \times 10^{-2}$	6–10	10–12	
Binary systems containing $(UO_2)_2[Fe(CN)_6]$-gelatin-immobilized matrix materials					
8-Mercaptoquinoline, 5-chloro-8-mercaptoquinoline and 5-thiomethyl-8-mercaptoquinoline (HL)					144, 147
$(UO_2)_2[Fe(CN)_6] + 4OH^- + 4H_2O \rightarrow 2(UO_2)(OH)_2(H_2O)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-5}	4–10	11–13	
$(UO_2)(OH)_2(H_2O)_2 + 2HL \rightarrow UO_2L_2 + 2H_2O$	0.1–1.0	2.0×10^{-2}–1.0×10^{-1}	6–10	11–13	
8-Hydroxyquinoline (HL)					144–146
$(UO_2)_2[Fe(CN)_6] + 4OH^- + 4H_2O \rightarrow 2(UO_2)(OH)_2(H_2O)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-5}	4–10	10–13	
$2(UO_2)_2\,[Fe(CN)_6] + 4OH^- \rightarrow [(UO_2)_2(OH)_2]_2[Fe(CN)_6] + [Fe(CN)_6]^{4-}$	0.4–2.0	1.0×10^{-4}–1.5×10^{-2}	<1	10–13	
$(UO_2)(OH)_2(H_2O)_2 + HL \rightarrow UO_2L(OH)(H_2O) + 2H_2O$	0.2–1.5	2.0×10^{-3}–2.0×10^{-2}	2–6	10–13	
$UO_2L(OH)(H_2O) + HL \rightarrow UO_2L_2 + 2H_2O$	0.5–1.0	2.0×10^{-2}–5.0×10^{-2}	4–10	10–13	
$UO_2L_2 + HL + OH^- \rightarrow [UO_2L_3]^- + H_2O$	0.1–0.5	$>8.0 \times 10^{-2}$	8–10	10–13	
5-Chloro-8-hydroxyquinoline (HL)					144, 146
$(UO_2)_2[Fe(CN)_6] + 4OH^- + 4H_2O \rightarrow 2(UO_2)(OH)_2(H_2O)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-5}	4–10	11–13	
$(UO_2)(OH)_2(H_2O)_2 + HL \rightarrow UO_2L(OH)(H_2O) + 2H_2O$	0.3–1.8	1.5×10^{-3}–2.5×10^{-2}	2–6	11–13	
$UO_2L(OH)(H_2O) + HL \rightarrow UO_2L_2 + 2H_2O$	0.1–0.5	5.0×10^{-2}–1.0×10^{-1}	4–10	11–13	
$UO_2L_2 + HL + OH^- \rightarrow [UO_2L_3]^- + H_2O$	0.1–0.5	$>1.0 \times 10^{-1}$	8–10	11–13	
5,7-Dichloro-8-hydroxyquinoline (HL)					144, 146
$(UO_2)_2[Fe(CN)_6] + 4OH^- + 4H_2O \rightarrow 2(UO_2)(OH)_2(H_2O)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-5}	4–10	10–13	
$(UO_2)(OH)_2(H_2O)_2 + HL \rightarrow UO_2L(OH)(H_2O) + 2H_2O$	0.2–1.7	1.2×10^{-3}–1.5×10^{-2}	1–3	11–13	
$UO_2L(OH)(H_2O) + HL \rightarrow UO_2L_2 + 2H_2O$	0.1–0.5	5.0×10^{-2}–1.0×10^{-1}	4–10	11–13	
8-Mercaptoquinoline, 5-chloro-8-mercaptoquinoline and 5-thiomethyl-8-mercaptoquinoline (HL)					144, 147
$(UO_2)_2[Fe(CN)_6] + 4OH^- + 4H_2O \rightarrow 2(UO_2)(OH)_2(H_2O)_2 + [Fe(CN)_6]^{4-}$	0.1–2.0	1.0×10^{-6}–1.0×10^{-5}	4–10	11–13	
$(UO_2)(OH)_2(H_2O)_2 + 2HL \rightarrow UO_2L_2 + 2H_2O$	0.1–1.0	2.0×10^{-2}–1.0×10^{-1}	6–10	11–13	

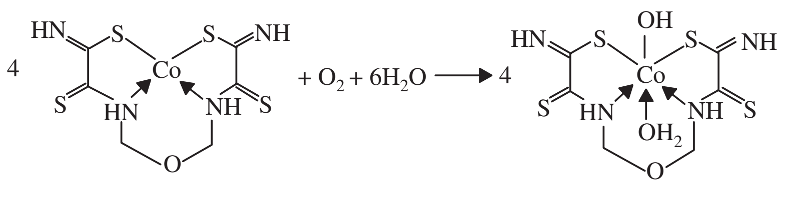
a mono- or polydentate ligand relative to the metal ion, facilitating a specific stereochemical orientation of the reagents. Such reactions are called template synthesis and the organic reagents are referred to as ligand synthons [59]. Significant numbers of similar reactions have been discovered and there are several books on this subject [150–157]. In the majority of cases, however, such reactions occur upon heating. Specific conditions in the metal hexacyanoferrate(II) gelatin-immobilized matrices, such as small reaction volume, may allow ligand synthons to come closer together favoring soft template synthesis where formation of chelate complexes proceeds at room temperature. Most template syntheses are classified as Schiff-base condensation [59], where intramolecular water molecules are formed at the expense of the mobile hydrogen atoms of one ligand synthon and the oxygen atoms of the other ligand synthon with subsequent dehydration. The probability of template synthesis rises as mobility of the hydrogen atoms in the ligand synthon becomes greater.

Gelatin molecules in alkaline medium have a negative charge [24–27]; therefore, proton-donating capability of the compounds immobilized in such gels are more pronounced than in aqueous solution. It thus follows that template synthesis in the metal hexacyanoferrate(II) gelatin-immobilized matrix should proceed more effectively than the same process in a solution or the solid phase [158–187]. Study of template synthesis in the triple **M**(II) - N, S-containing ligand synthon - O-containing ligand synthon (**M** = Co, Ni, Cu) and in the **M**(III) - N,S-containing ligand synthon - O-containing ligand synthon dithiooxamide (**M** = Co) testify in favor of such a conclusion. These studies show that when N,S-containing ligand synthon is dithiooxamide $H_2N{-}C({=}S){-}C({=}S){-}NH_2$ and the O-containing ligand synthon is formaldehyde $H_2C{=}O$, in the $Co_2[Fe(CN)_6]$-gelatin-immobilized matrix at pH>11, the process described by equation (26) takes place [158, 159].



(26)

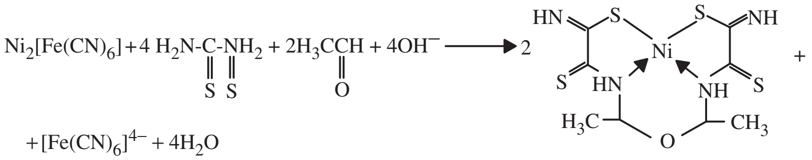
The Co(II) complex, however, is intermediate and immediately oxidized to heteroligand Co(III) containing an inner coordination sphere (N,N,S,S)-tetradentate chelating ligand-2,8-dithio-3,7-diaza-5-oxanonandithioamide-1,9 and monodentate ligands OH and H_2O, according to equation (27) [158, 159].



(27)

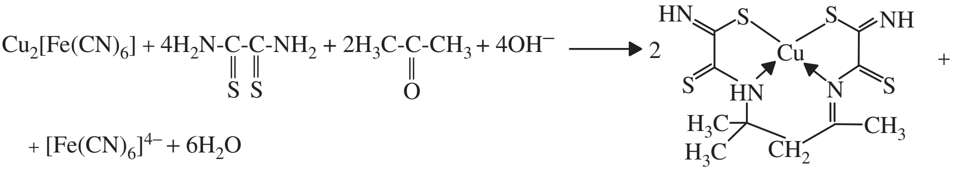
Template processes similar to (26) occur in the M(II)-dithiooxamide-formaldehyde systems upon complexation in the $Ni_2[Fe(CN)_6]$-gelatin-immobilized matrix [160–163] and $Cu_2[Fe(CN)_6]$ one [161, 163–165]. However, complexes of M(II) are final products of such a synthesis. As in the case of nucleophilic substitution in the copper(II) hexacyanoferrate(II) matrix, alkaline destruction $Cu_2[Fe(CN)_6] \rightarrow Cu(OH)_2$ precedes the template reaction. Upon contact of the $KCo[Fe(CN)_6]$-gelatin-immobilized matrix with water solutions containing dithiooxamide and formaldehyde, template is observed [166]; the final product of such a synthesis is the same as in equation (27).

Template processes proceeding in the Ni(II)-dithiooxamide-axcetaldehyde system with complexation in the $Ni_2[Fe(CN)_6]$-gelatin-immobilized matrix were studied [165], equation (28).



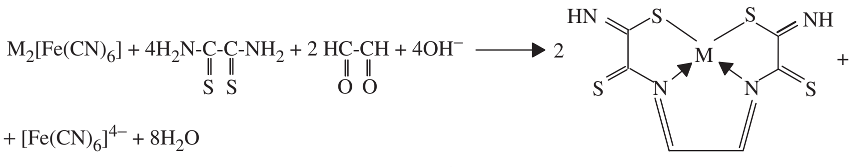
(28)

The structure of the final product of such a synthesis is similar to the final product formed in Ni(II)-dithiooxamide-formaldehyde, differing only by two methyl groups. The similar process occurs in the Cu(II)-dithio-oxamide-acetaldehyde system with complexation in the $Cu_2[Fe(CN)_6]$ matrix [166]. However, changing acetaldehyde to acetone, chelate complexes with (N,N,S,S)-donor ligand, which does not contain oxygen atoms, are formed [166, 168–171], equation (29) [170].



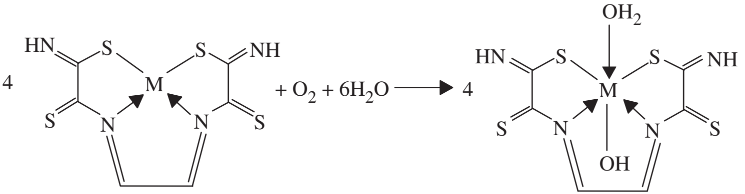
(29)

The ligand synthon may be an organic compound such as glyoxal (O=)HC–CH(=O) containing two carbonyl groups [172–176]. The template processes for M(II)-dithiooxamide-glyoxal systems in the corresponding $M_2[Fe(CN)_6]$-gelatin-immobilized matrices (M = Co, Ni, Cu) may be described by equations (30–31) [172–175].



(30)

(M = Co, Ni, Cu)

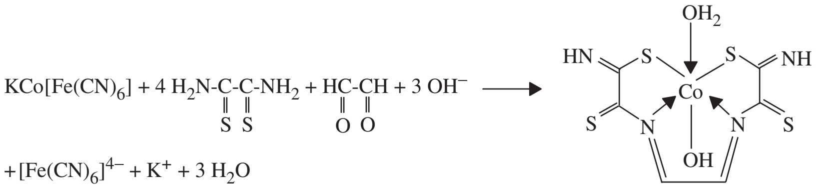


(31)

(M = Co)

The final product of the template synthesis for the Co(III)-dithiooxamide-glyoxal system proceeding in the $KCo[Fe(CN)_6]$ matrix is the same as for the

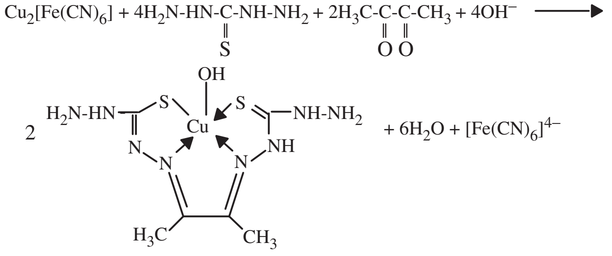
Co(II)-dithiooxamide-glyoxal in $Co_2[Fe(CN)_6]$ [176], equation (32):



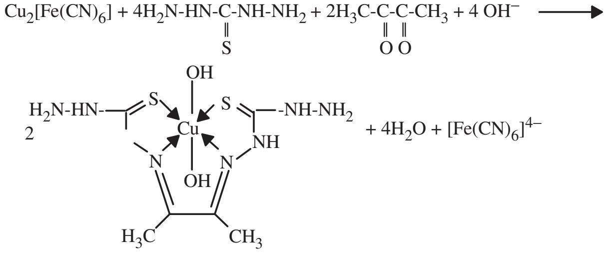
(32)

Reports on the possibility of template synthesis in at least one of these systems are lacking; moreover, dithiooxamide, despite its four mobile hydrogen atoms, has not been used as a ligand synthon in template synthesis.

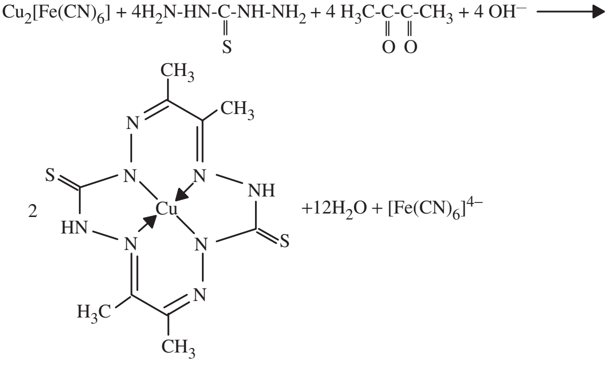
As other ambidentate (N,S) ligand synthons, thiocarbohydrazide $H_2N–NH–C(=S)–NH–NH_2$ and dithiomalonamide $H_2N–C(=S)–NH–C(=S)–NH_2$ were used [177–179] and [180, 181], respectively. In many cases when a ligand synthon was used, formation of several coordination compounds occurred. In the Cu(II)-thiocarbohydrazide-diacetyl triple system three template complexes were formed, equations (33–35) [177, 179].



(33)

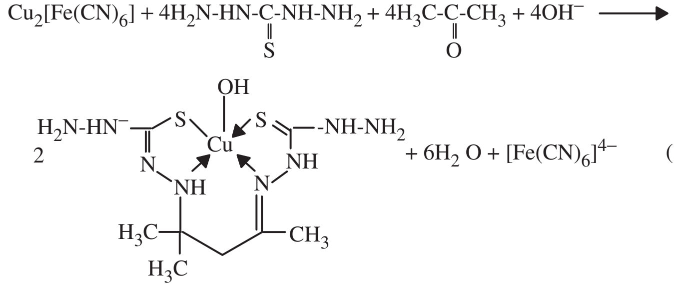


(34)



(35)

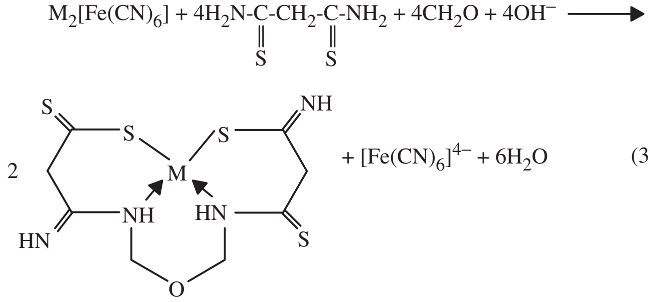
However, in the Cu(II)-thiocarbohydrazide-acetone [178] and M(II)-dithiomalonamide-formaldehyde systems ($M = Ni$, Cu) [180] only one template complex is formed, as shown in equations (36) and (37), respectively.



$$Cu_2[Fe(CN)_6] + 4H_2N\text{-}HN\text{-}\underset{\substack{\|\\ S}}{C}\text{-}NH\text{-}NH_2 + 4H_3C\text{-}\underset{\substack{\|\\ O}}{C}\text{-}CH_3 + 4OH^- \longrightarrow$$

$$+ 6H_2O + [Fe(CN)_6]^{4-}$$

(36)



$$M_2[Fe(CN)_6] + 4H_2N\text{-}\underset{\substack{\|\\ S}}{C}\text{-}CH_2\text{-}\underset{\substack{\|\\ S}}{C}\text{-}NH_2 + 4CH_2O + 4OH^- \longrightarrow$$

$$+ [Fe(CN)_6]^{4-} + 6H_2O$$

(37)

The $D^{\blacktriangledown} = f(C_F, C_L^{\circ}, t)$ relationships are presented in figure 6.

The products of template synthesis in the triple systems proceeding in the gelatin-immobilized matrices differ from products in the same triple systems proceeding in solution or solid phase. The products of complexation processes proceeding in the **M**(II)–(N,S)-containing ligand synthon – O-containing ligand synthon in solutions or solid phase and in the corresponding $\mathbf{M}_2[Fe(CN)_6]$-gelatin-immobilized matrix ($\mathbf{M} = Co$, Ni, Cu) are presented in table 4. The template synthesis in triple systems of metal hexacyanoferrate(II) gelatin-immobilized matrix differ extremely from the results of template synthesis in solution or solid phase. In most cases, the template synthesis in gelatin-immobilized matrix is accompanied by formation of more complex coordination compounds than template synthesis in solution or solid phase; exceptions to this are only Ni(II)-thiocarbohydrazide-acetone, Ni(II)-thiocarbohydrazide-diacetyl and Ni(II)-dithiomalonamide-diacetyl triple systems where template synthesis into $Ni_2[Fe(CN)_6]$-gelatin-immobilized matrix is not realized at all (perhaps, owing to that nickel(II)-hexacyanoferrate(II) is more stable in comparison with nickel(II) complexes with thiocarbohydrazide which are intermediates in the template reaction).

An attempt to interpret the results in table 4 with use of quanto-chemical rated methods was undertaken [183]. Lengths of chemical bonds and valence angles for template complexes formed in the triple systems, table 4, and also values of Gibbs's energy ΔG^0_{298} for corresponding template processes were calculated. It was established that in systems where these processes take place, ΔG^0_{298} values calculated for metal

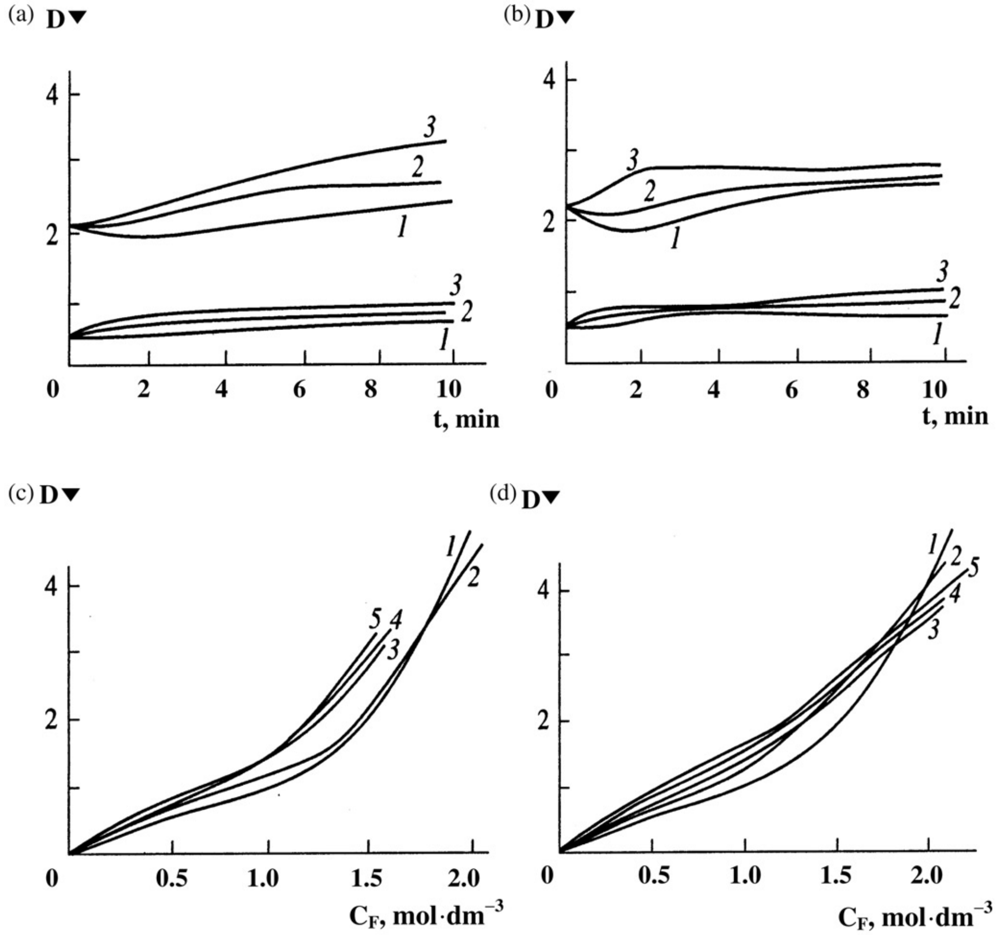
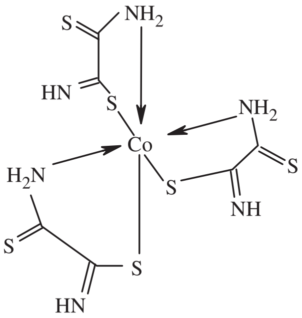
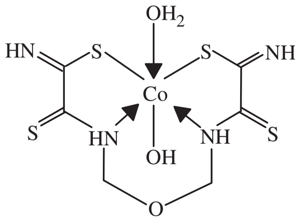
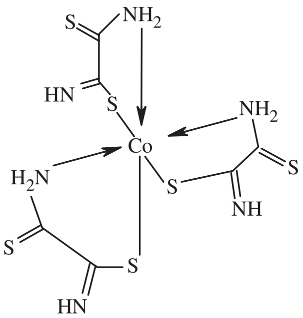
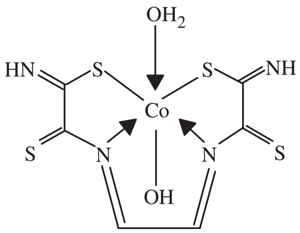
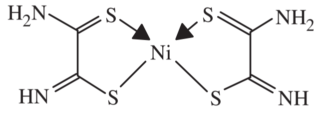
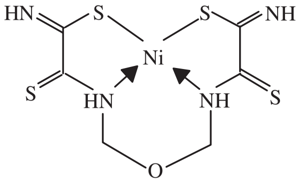
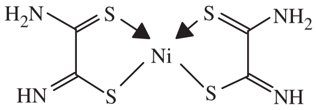
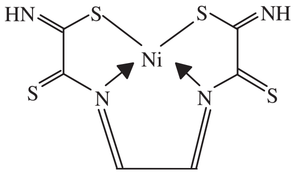
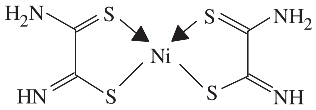
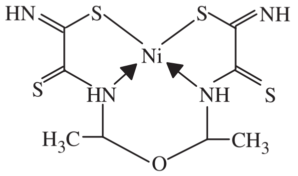


Figure 6. Original $D^{\blacktriangledown} = f(C_F, C^{\circ}_L, t)$ relationships in the $Cu_2[Fe(CN)_6]$-dithiooxamide-glyoxal triple system [172] for dithiooxamide: glyoxal molar ratio 0.50 (a, b) and 1.00 (c, d) in the coordinated section $[C_F = \text{const}$, varied C°_L, argument $t]$ (a, c) and in the coordinated section $[C^{\circ}_L = \text{const}$, varied t, argument $C_F]$ (b, d). (a, c) at $C_F = 0.50\,\text{mol dm}^{-3}$ and $1.55\,\text{mol dm}^{-3}$ for $C^{\circ}_L = 3.0 \times 10^{-3}\,\text{mol L}^{-1}$ (1), $6.0 \times 10^{-3}\,\text{mol L}^{-1}$ (2) and $1.2 \times 10^{-2}\,\text{mol L}^{-1}$ (3); (b, d) at $C^{\circ}_L = 6.0 \times 10^{-3}\,\text{mol L}^{-1}$ and $t = 1$ min (1), 2 min (2), 4 min (3), 6 min (4), 10 min (5). The optical densities have been measured using a blue filter with a transmission maximum at 450 nm.

chelate cycles are usually negative; in systems where such processes were not observed, ΔG^0_{298} values calculated are positive. So, for process of template stitch in Cu(II)-thiocarbohydrazide-formaldehyde, Cu(II)-thiocarbohydrazide-acetone and Cu(II)-thiocarbohydrazide-diacetyl triple systems where the template process is obtained in solution and in the copper(II) hexacyanoferrate(II) gelatin-immobilized matrix, ΔG^0_{298} values calculated are −53.79, −18.26 and −136.81 kJ, respectively. In Cu(II)-dithiomalonamide-diacetyl triple system where the template process in solution is absent, $\Delta G^0_{298} = +22.95$ kJ. The good agreement between calculated and experimental

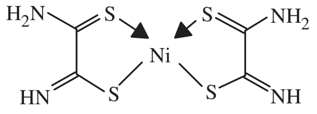
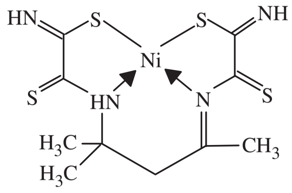
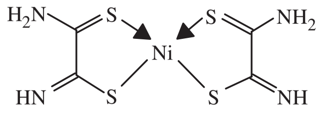
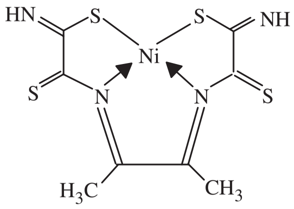
Table 4. The products of complexing processes proceeding in the M(II)- (N,S)-containing ligand synthon-O-containing ligand synthon in the solutions or solid phase and in the $M_2[Fe(CN)_6]$-gelatin-immobilized matrix.

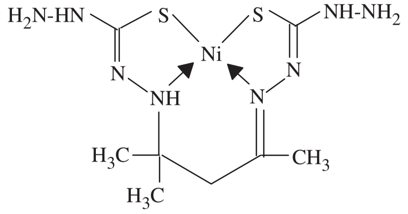
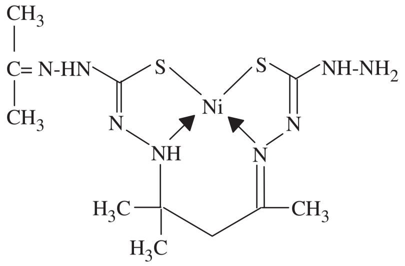
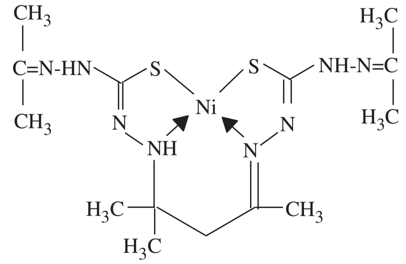
Triple system	Products of complexing processes		Ref.
	In solution or solid phase	In gelatin-immobilized matrix	
1	2	3	4
Triple systems containing Co(II)			
Co(II)-dithiooxamide-formaldehyde			158, 159, 163, 167
Co(II)-dithiooxamide-glyoxal			158, 159, 173

Triple systems containing Ni(II) Ni(II)-dithiooxamide-formaldehyde			160–163, 168, 169, 175
Ni(II)-dithiooxamide-glyoxal			162, 169, 174
Ni(II)-dithiooxamide-acetaldehyde			165, 168, 175

(*Continued*)

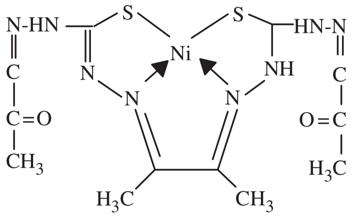
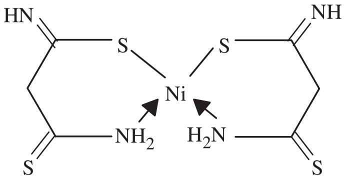
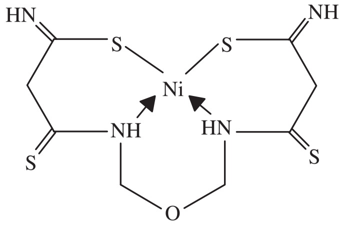
Table 4. Continued.

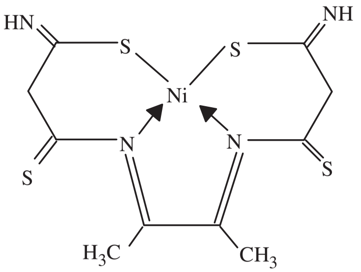
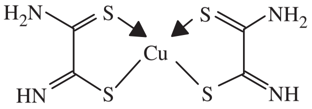
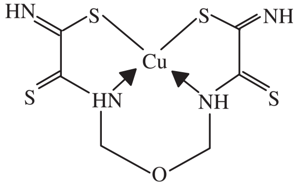
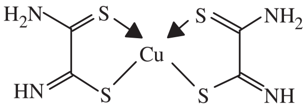
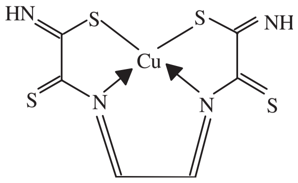
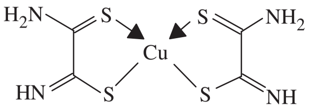
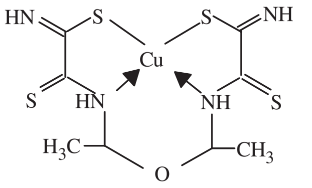
Triple system	Products of complexing processes		Ref.
	In solution or solid phase	In gelatin-immobilized matrix	
1	2	3	4
Ni(II)-dithiooxamide-acetone			168, 171, 175
Ni(II)-dithiooxamide-diacetyl			174, 175

Ni(II)-thiocarbohydrazide-acetone	  	–	182

(*Continued*)

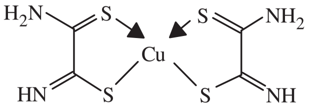
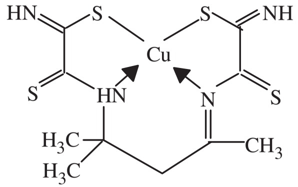
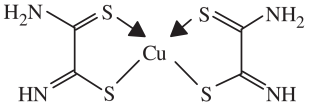
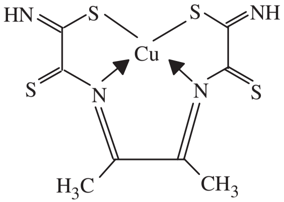
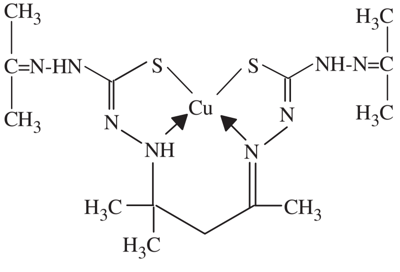
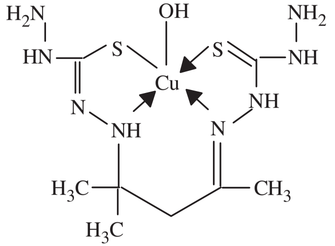
Table 4. Continued.

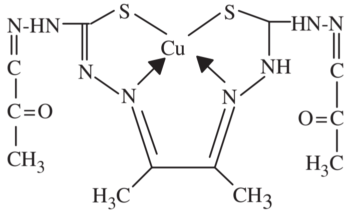
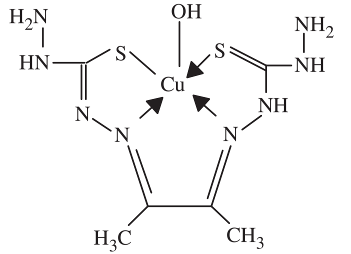
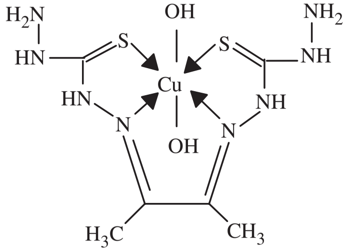
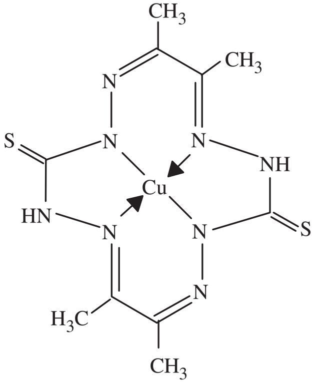
Triple system	Products of complexing processes		Ref.
	In solution or solid phase	In gelatin-immobilized matrix	
1	2	3	4
Ni(II)-thiocarbohydrazide-diacetyl		–	179, 183
Ni(II)-dithiomalonamide-formaldehyde			180

Ni(II)-dithiomalonamide-diacetyl		–	181
Triple systems containing Cu(II)			
Cu(II)-dithiooxamide-formaldehyde			163, 164, 166, 169
Cu(II)-dithiooxamide-glyoxal			169, 172
Cu(II)-dithiooxamide-acetaldehyde			166

(*Continued*)

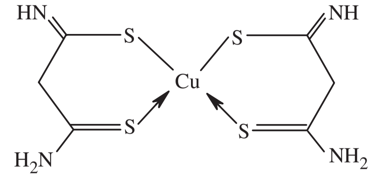
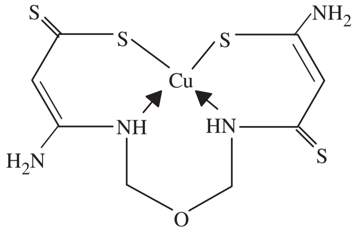
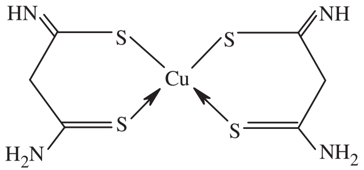
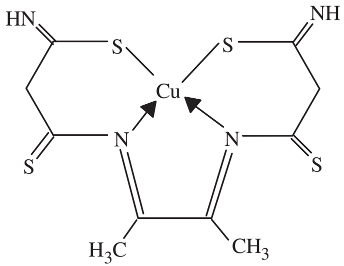
Table 4. Continued.

Triple system	Products of complexing processes		Ref.
	In solution or solid phase	In gelatin-immobilized matrix	
1	2	3	4
Cu(II)-dithiooxamide-acetone			166, 170
Cu(II)-dithiooxamide-diacetyl			172
Cu(II)-thiocarbohydrazide-acetone			178

Cu(II)-thiocarbohydrazide-diacetyl		  	177, 179

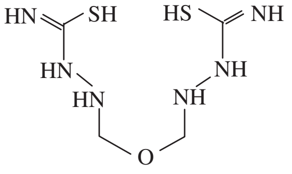
(*Continued*)

Table 4. Continued.

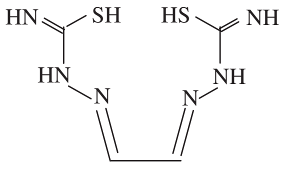
Triple system	Products of complexing processes		Ref.
	In solution or solid phase	In gelatin-immobilized matrix	
1	2	3	4
Cu(II)-dithiomalonamide-formaldehyde			180
Cu(II)-dithiomalonamide-diacetyl			181

values of constants of superthin interaction a_{Cu} and a_N in the ESR spectra of template complexes should be noted. For a product of template synthesis in the Cu(II)-thiocarbohydrazide-diacetyl triple system, calculation gives a_{Cu} of 77 mT and a_N of 15.8 mT, whereas experimental values are 89 and 16.0 mT, respectively [183]. As one would expect, plane rhombic template Ni(II) complexes formed in all triple systems under examination having $M_S = 1$ are stable in comparison with similar Ni(II) complexes having $M_S = 3$. For example, in the Ni(II)-thiocarbohydrazide-diacetyl triple system ΔG^0_{298} for reaction of formation of metal complex with $M_S = 1$ $\Delta G^0_{298} = -152.24$ kJ, whereas for $M_S = 3$ $\Delta G^0_{298} = -128.66$ kJ. Plane rhombic Ni(II) and Cu(II) complexes in all cases are calculated to be stable in comparison with similar tetrahedral complexes.

Template processes analogous to reactions (23–24) and (27–28) most likely take place, also, in the M(II)-thiosemicarbazide ($H_2N–C(=S)–NH–NH_2$)– formaldehyde and M(II)-thiosemicarbazide-glyoxal systems (M = Co(II), Ni(II), Cu(II)) [184–186]. As a result of these processes, coordination compounds of cobalt(III), nickel(II) and copper(II) with 2,3,7,8-tetraaza-5-oxanonan-dithioamide-1,9 (formula **III**) and 2,3,6,7-tetraazaoctadien-3,5-dithioamide-1,8 (formula **IV**) are formed.



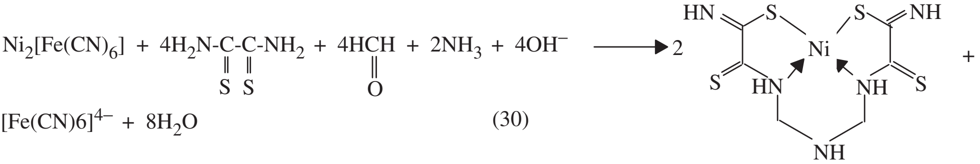
III



IV

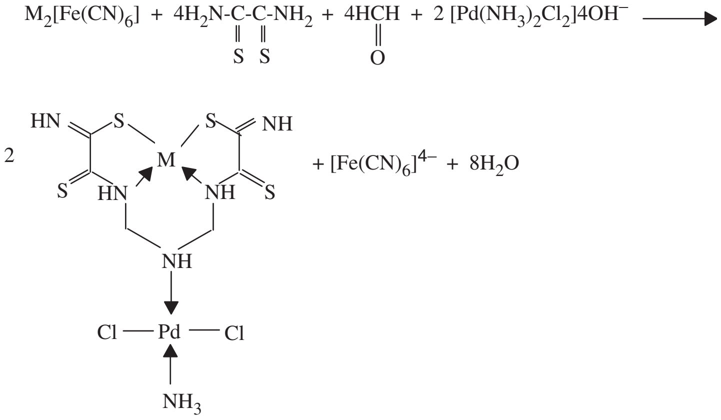
However, further studies are required yet to confirm this conclusion.

The possibility of soft template synthesis in the quarter Ni(II)-dithiooxamide-formaldehyde-ammonia system proceeding in the $Ni_2[Fe(CN)_6]$-gelatin-immobilized matrix according to equation (38) was examined [188].

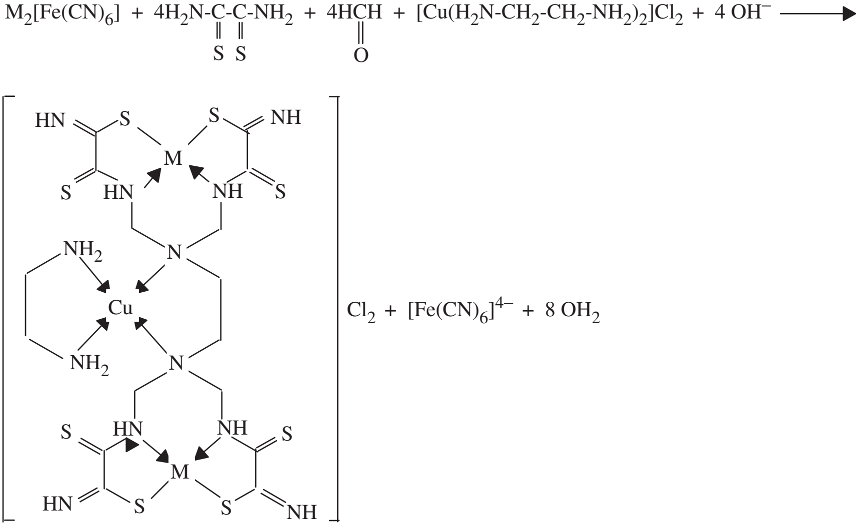


$$Ni_2[Fe(CN)_6] + 4H_2N\text{-}\underset{\|}{\overset{}{C}}\text{-}\underset{\|}{C}\text{-}NH_2 + 4H\underset{\|}{C}H + 2NH_3 + 4OH^- \longrightarrow 2\,[\ldots] + [Fe(CN)6]^{4-} + 8H_2O \qquad (30)$$

Although investigations are only beginning, there are grounds to believe that the potential of template synthesis in the metal hexacyanoferrate(II) gelatin-immobilized matrices is high, and the list of triple and quarter systems with metal ion-ligand synthons where it may be realized, can be significantly extended. For example, ligand synthons may be combinations (acetylacetone + 1,2-ethylenediamine), (1-amino-2-thion-1-propanone + 1,3-propilenediamine). A ligand synthon with some coordination compound with ligands having donor atoms containing mobile hydrogen atoms, diaminodichloropalladium(II) $[Pd(NH_3)_2Cl_2]$ or *bis*(1,2-ethylenediamino)copper(II) dichloride $[Cu(H_2N–CH_2–CH_2–NH_2)_2]Cl_2$ (schemes 1 and 2, respectively) [189] may be expected:

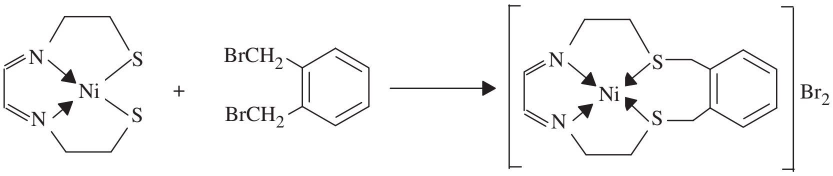


Scheme 1.



Scheme 2.

Specific conditions produced in the metal hexacyanoferrate(II) gelatin-immobilized matrix systems favor reactions of template synthesis that are quite unique for today, such as the Bush synthesis [59, 150–157], for example scheme 3,



Scheme 3.

in the course of which chemical bonds are formed between sulfurs of the metal chelate rings and carbon atoms of the methylene groups that are bound to the benzene ring.

4. Applications

Gelatin-immobilized matrix materials may be used in the same fields of science and industry as materials based on other polymer-immobilized systems with fixing of immobilized substance by chemical bonds with the functional groups of polymer [3–5]. However, there are specific aspects of their application which follow directly from the properties of the systems.

First, since silver-halide gelatin-immobilized matrix materials are precursors of metal complex ones, complexation in the gelatin-immobilized matrix may be used for formation of *silverless photographic images* on AgHal-photographic materials (especially on radiographic films intended for registration of hard ionizing radiation with high content AgHal per unit of surface of photographic layer). Silver economy in the chemico-photographic industry which consumes about 20% of silver mined in the world may be realized.

Second, since they have nanostructured organization of immobilized substance and contain highly-dispersed chemical compounds, there is possibility to use such systems as *effective sorbents* of organic as well as inorganic substances. In this connection, the possibility exists for using gelatin-immobilized matrices as the immobile phase in various versions of chromatography.

Third, because all are optically isotropic and nanostructured objects, they may be used to obtain *absorption spectra* of immobilized chemical compounds contained in these matrices. This is particularly important when the compound to be analyzed is poorly soluble in water and organic solvents.

Fourth, as, on the one hand, reaction centers of gelatin-immobilized matrices are identical and are equally available for reagents, on the other hand, these matrices are independent phases in reaction systems and may be used as *effective catalysts* combining merits of catalysts for homogeneous and heterogeneous catalysis.

Fifth, since polymer-immobilized matrix materials are considered a sort of membrane, there is a possibility of using of them as immobilized membrane *ion-selective electrodes*.

Sixth, since these systems are tiny and, at the same time, owing to their high dispersity and sensitivity, may be used in analytical reactions, there is the possibility of using them as *sensor systems* for various chemical compounds.

These possible applications are discussed in detail in the following sections.

4.1. *Synthesis of silverless photographic images*

The process for formation of silverless photographic images consists of three stages:

- bleaching of the silver image obtained on the photographic material by means of standard treatment [34, 35] in a solution containing potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$, the soluble salt of a 3*d*-element ion (as a rule, the chloride or sulfate), and any organic hydroxyacid (citric, oxalic or tartaric);

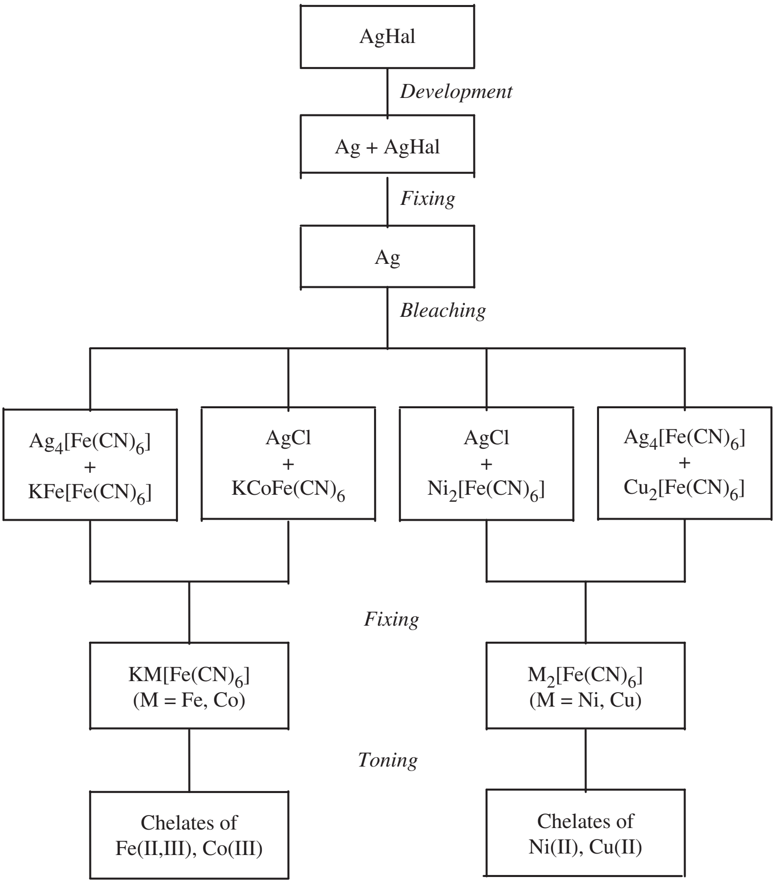


Figure 7. The general scheme of formation of metal chelate silverless photographic images on the AgHal photographic materials.

- fixing of the bleached image by treating the photographic layer with an aqueous solution of sodium thiosulphate $Na_2S_2O_3$;
- toning of the image by treating the photographic layer with an alkaline solution of the corresponding chelating organic compound.

The general scheme of obtaining images is shown in figure 7. In terms of the composition of the solutions used to treat the photographic materials and the chemistry of the processes occuring, the first two stages correspond to the synthesis of metal hexacyanoferrate(II) gelatin-immobilized matrices and the third to the complexation with participation of these matrices [190–192]. In a number of instances silverless photographic images from metal chelates can be produced by a shorter procedure; the exposed silver halide photographic material is initially developed and then subjected to treatment involving the successive operations indicated above. It is then possible to shorten the time required to obtain the silverless metal chelate image and to improve the efficiency and accelerate oxidation of the elemental silver to the corresponding silver(I) compounds ($Ag_4[Fe(CN)_6]$ or AgCl) [192]. Technological processes of this type have been described in the literature [141, 193–230]. Most of these publications have been

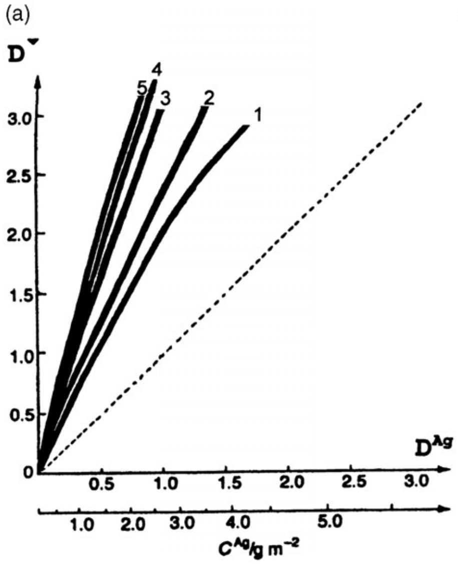


Figure 8. Original $D^{\blacktriangledown} = f(D^{Ag})$ kinetic curves of formation of silverless photographic images consisting of Fe(III) chelates with 5-bromo-8-mercaptoquinoline at $C^{\circ}_{L} = 2.5 \times 10^{-2}$ (a) and 5.0×10^{-2} (b) mol L^{-1}, $t = 1$ min (1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5) [141]. The optical densities D were measured using a blue filter with a transmission maximum at 450 nm. The dependence $D^{\blacktriangledown} = f(D^{Ag})$ for initial silver image has been shown as (…).

devoted to synthesis of silverless images from Ni(II) chelates [193–208]; a somewhat smaller number have been devoted to silverless images consisting of Cu(II) chelates [209–222]. Silverless images obtained from other metal chelates are less observed [141, 223–230]. In particular, technologies for the production of silverless images consisting of Ni(II) chelates with dimethylglyoxime [190–193], 8-mercaptoquinoline [194–197], dithiooxamide and *N*,*N*′-diphenyldithiooxamide [198–205], quinoxaline-2,3-dithiol [204], *N*,*N*′-diphenylthiooxamide [207], macrocyclic ligand-2,8-dithio-3,7-diaza-5-oxa-nonandithioamide-1,9 [208], Cu(II) chelates with α-benzoinoxime [215, 217], dithio-oxamide [190–192, 209, 210], 1,2-dithiocarbamylhydrazine [212], some bulky 3-benzoylthioureas [218–222], Co(II) chelates with nitrosonaphthols [223, 224], Co(III) chelates with dithiooxamide [225–227], Fe(III) chelates with various 8-mercaptoquinolines [141] and even UO_2(VI) with 8-mercaptoquinoline [230] have been elaborated. The typical kinetic curves of formation for silverless photographic images are presented in figure 8.

The formation of silverless images consisting from Ni(II) chelates with dithiooxamide is most interesting [198–205]. It has been used, for example, for the preparation of blue slides [199–201]. The procedure for the preparation of blue slides is less laborious and, less demanding as regards external conditions compared with the familiar traditional process based on organic dyes [199–201]. The blue or ultramarine images obtained from $[Ni(HL)_2]_n$ chelate (H_2L is dithiooxamide) are distinguished by a greater purity of light lines, and greater photostability. Yet another important quality of this procedure is that, in contrast to all other processes for the intensification of photographic images known hinherto [34, 35], in many cases it does not increase but actually diminishes the

Table 5. Resolvometric parameters of silverless photographic images consisting of metal chelates [211].

Metal chelate forming silverless image	Resolvometric ability R (mm^{-1})	Resolvometric width l, units of optical density
Fe(III) with 8-mercaptoquinoline	165	0.22
Co(III) with dithiooxamide	115	0.20
Co(III) with 8-mercaptoquinoline	135	0.26
Co(III) with *N*,*N*′-diphenyldithiooxamide	125	0.25
Ni(II) with dithiooxamide (blue)	145	0.33
Ni(II) with dithiooxamide (violet)	120	0.30
Ni(II) with 8-mercaptoquinoline	120	0.35
Ni(II) with quinoxaline-2,3-dithiol (pink-red)	120	0.27
Ni(II) with quinoxaline-2,3-dithiol (green-blue)	145	0.39
Ni(II) with *N*,*N*′-diphenyldithiooxamide	155	0.35
Cu(II) with dithiooxamide	190	0.22
Cu(II) with 8-mercaptoquinoline	185	0.32
Cu(II) with quinoxaline-2,3-dithiol	180	0.22
Cu(II) with 1,2-dithiocarbamoylhydrazine	195	0.25
Cu(II) with α-benzoinoxime	200	0.40
Initial silver image	195	0.44

degree of fog density compared with the initial silver image [198–205]. The cause of this phenomenon has been discussed [199–201].

The phenomenon indicated is fairly typical for technologies for the synthesis of silverless images from chelates of 3*d*-elements, observed, for example, in the formation of silverless images from Cu(II) chelate complexes with dithiooxamide (dark-green) [190–192, 209, 210], Cu(II) chelates with 1,2-dithiocarbamoylhydrazine (black) and (1-carbamoyl-2-carbamoyl)hydrazine [212] and Co(III) chelates with dithiooxamide (amber-yellow) [225–227]. The images generated by the copper(II) chelate complex with 1,2-dithiocarbamoylhydrazine and iron(II) chelate with 8-hydroxyquinoline [229] are very close to the initial neutral grey silver images. This is particularly effective in those cases where, after intensification, it is desirable to retain the black or grey-black color of the image.

The problem of quality of silverless metal chelate photographic images was discussed [211], where resolvometric parameters of these images had been measured. It was found that, although some decrease of these parameters occurs, in most cases it is acceptable from the practical point of view table 5. Moreover, in some cases (for example, Cu(II) chelate with α-benzoinoxime) these parameters were found even higher than for the initial silver image.

Employment of all these technologies makes it possible to widely vary the photographic characteristics of the treated materials. In particular, by altering the concentrations and duration of the toning stage, it is possible to both decrease and increase the photographic sensitivity achieved in the formation of the initial silver image [192]. Review articles have been published on this issue [192, 231, 232].

4.2. *Gelatin-immobilized sorbents*

The second field of application of metal complex gelatin-immobilized matrix materials is their use in sorption processes where these systems may be highly-effective sorbents of various metal ions owing to their participation in ionic exchange reactions proceeding

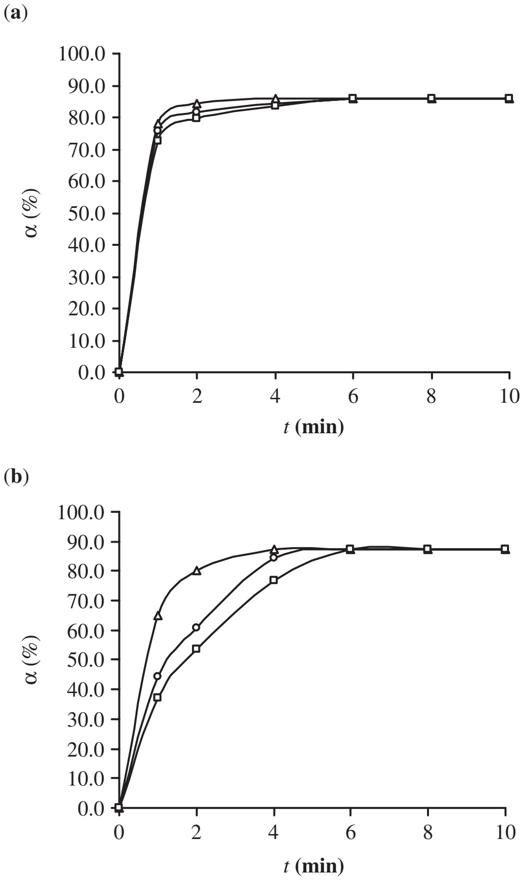


Figure 9. Original relationships $\alpha(t)$ for the sorption processes of Cd(II) with $Co_2[Fe(CN)_6]$-gelatin-immobilized matrix (a) [89] and Cu(II) with $Mn_2[Fe(CN)_6]$ [87] (b). Concentration of Cd(II) and Co(II) in solutions is 7.0×10^{-2} mol L^{-1}. (a): $C_F = 0.19$ mol dm^{-3} (–o–o–o–), 0.40 (–Δ–Δ–Δ–) and 0.70 mol dm^{-3} (–□–□–□–); (b) $C_F = 0.40$ (–o–o–o–), 1.00 (–Δ–Δ–Δ–) and 1.90 mol dm^{-3} (–□–□–□–).

into the gelatin matrix [55]. The possibility of such reactions with participation of solid-phase metal hexacyanoferrates(II) (which, as was mentioned above, are related to metal complexes immobilized in gelatin most easily) was noticed in 1935. It was found subsequently that compounds indicated have good selectivity regarding sorption of alkaline ions [108]. Doubtless metal hexacyanoferrates(II) are capable to be sorbents of *p*-, *d*- and *f*-element ions, and sorption ability of metal hexacyanoferrates(II) gelatin-immobilized matrices must be higher than sorption ability of solid-phase metal hexacyanoferrates(II). However, publications confirming this appeared only recently [87, 89, 90, 92, 93, 95, 97, 98, 100, 101, 103, 104]. Sorption processes of 3*d*- and 4*d*-element ions by metal hexacyanoferrate(II) gelatin-immobilized matrices accompanied with $M(II) \rightarrow M'(II)$, $M(III) \rightarrow M'(II)$ or $M(II) \rightarrow M'(III)$ ionic exchange, proceeds considerably faster than analogous processes in solid-phase metal hexacyanoferrates(II). Some results concerning sorption of *d*-element ions by various metal hexacyanoferrates(II) have been presented in figure 9. In most cases this process is near completion within 5 min. Limited degree of sorption α_{max} is dependent on the nature of the metal hexacyanoferrate(II) and M′; sorption by copper(II) hexacyanoferrate(II) fluctuated from 19% (Cd) to 31% (Co) [55, 89], sorption by iron(III) hexacyanoferrate(II) from 12% (Ni) to 40% (Cu) [55, 103], and sorption by manganese(II) hexacyanoferrate(II) from 36% (Cd) to 95% (Ni) [55, 87]. It is significant that α_{max} does not depend on metal hexacyanoferrate(II) concentration in gelatin massif for one sorption system, though as a whole $\alpha(t)$ is weak, but nevertheless traced (figure 9).

There are many publications concerning use of some *p*- and *d*-elements prepared by chemical sedimentation from either complexing reactions between M(II) (M = Pb, Cu, Fe, Zn, Mn) and any (N,S)-donor organic reagent (thioacetamide, thiourea, thiosemicarbazide, etc.) in alkaline environment, or interaction of the named ions with Na_2S, K_2S and $(NH_4)_2S$ at room and lower temperatures, as sorbents of thin-film sulfides [233–240]. The technology of obtaining gelatin-immobilized metal sulfides from appropriate gelatin-immobilized metal hexacyanoferrates(II), however, was described only recently [55, 64] and their sorption properties are just beginning to be studied [241, 242]. However, preliminary investigation indicates the much greater efficiency of metal sulfide gelatin-immobilized sorbents in comparison with microcrystalline thin films of analogous metal sulfides. In particular, the degree of conversion (replacement) of the appropriate ion on Ag(I) in 1 day for sorbents based on PbS-**GIM** is 90%, whereas for a similar thin-film metal sulfide does not reach 10% [241].

An interesting application of gelatin-immobilized metal complexes is as a motionless phase in chromatography as a sorbent. By taking into consideration properties of gelatin as polymeric massif [55], it can be expected that gelatin-immobilized metal complexes will have particular application in thin-layer liquid-gel chromatography. This potential, however, has remained unrealized until now.

4.3. *Preparation of test-objects for the measurement of absorption spectra*

It would be desirable to have standard reference samples of individual chemical compounds with recorded absorption spectra. Such samples (test-objects), however, should meet a number of specific requirements:

- their spectra should coincide with the spectrum of the individual compound under study;
- optical characteristics of reference samples should remain unchanged for a long time (as a minimum, several years), at least under certain favorable conditions;
- reference samples should be convenient to use;
- procedures for sample preparation should be as cheap and simple as possible.

In this connection, a fundamentally novel variant in preparation of test-objects for the measurement of UV-VIS and IR absorption spectra has been elaborated with the aid of complexing processes in metal hexacyanoferrate(II) gelatin-immobilized matrix systems. Its significant features reduce due to the fact that the substance analyzed is synthesized in a gelatin layer as a result of a series of specific chemical reactions [243–246]. The test-objects obtained using this method fully meet each requirement indicated above. In particular, test-objects containing coordination compounds of nickel(II) with dimethylglyoxime, copper(II) with dithiooxamide, cobalt(II) with 2-nitrozo-1-naphthol, iron(II) with 8-hydroxyquinoline, and dioxouranyl(VI) with 8-mercaptoquinoline have been prepared this way.

In principle, the ideas underlying this method can be used to prepare test-objects comprising a series of other inorganic compounds, for example oxides and sulphides [243, 246]. This method is also fairly promising for preparation of test-objects containing certain organic compounds which absorb intensively in the UV-VIS and IR spectrum region [245].

4.4. *Other promising possibilities*

Another aspect in which application of metal complex gelatin-immobilized matrix systems look promising is metal complex catalysis. There are two basic types of catalysts – so-called homogeneous and heterogeneous (intended for realization of homogeneous and heterogeneous chemical processes, respectively) [2, 5], having different sets of properties useful for catalysis. Stability, good reproducibility of results, high activity and selectivity are inherent in homogeneous processes; all of the catalytica centers are identical, available to reagents, and their activity depends on ligand environments and can be purposefully varied. In heterogeneous catalysts, usually only a small set of catalytic centers catalyze the reaction necessary, whereas others are inactive or catalyze undesirable parasitic processes. However, after catalytic reactions the catalyst must be separated from products. In homogeneous catalysis this is a serious problem, whereas with heterogeneous catalysts it is much easier. Creation of catalysts combining useful properties of both types of catalytic systems is one problem of modern catalysis. One approach is immobilization of catalytic active metal complexes in various polymeric masses [2, 5]. Heterogeneous metal complex catalysts which have characteristics closer to homogeneous catalysts are obtained in this case. They are synthesized with usual low-molecular metal complexes either by substitution of their ligands with functional groups of a polymeric massif or introduction of these metal complexes into cavities of the polymer. Such catalytic centers are identical as for homogeneous catalysts. They are also active in conditions close to those for homogeneous catalysts (in particular, at temperatures 300–350 K). Catalytically active centers of immobilized catalysts have a known structure enabling better understanding of the mechanism of catalytic reaction; such understanding brings us closer to the transition from empirical selection of catalysts to scientifically-grounded prediction of catalytic influence both in qualitative and quantitative aspects.

The majority of chemical reactions proceeds in solutions, especially water. It would be useful to have quasi-homogeneous metal complex catalysts, catalyzing chemical processes in water bound to a hydrophilic polymer, permeable for molecules of the solvent. Gelatin falls into such polymers with topographical parameters suitable for formation of metal complex catalytic systems. It is easy to form gels and gelatin swells in water solutions having various pH values, making cavities available for various substrates. What is more, it may be expected that in homogeneous catalysis with immobilized metal complexes, coordination complexes whose solubility in water does not allow use in homogeneous catalytic reactions, could be used. Regretfully potential opportunities of metal complex gelatin-immobilized matrix systems in catalysis have remained unpublished until now.

Achievements have been made in the field of enzyme processes as a kind of homogeneous catalysis mimicked by immobilized coordination compounds. In numerous biochemical reactions metal-enzymes participate with either a connected metal ion or show maximal activity upon introduction of a metal ion. These metal enzymes are high-molecular weight compounds having albuminous nature, with active centers including transition metals. In organisms they are included in biological membranes and can be considered as immobilized metal complexes in a gel matrix. The successes achieved recently in such systems led to search of highly-effective catalysts similar to biocatalysts. Since gelatin is known to be a low-molecular weight polypeptide, metal chelate gelatin-immobilized matrices may be catalysts similar to enzyme processes. This application of matrix systems, however, also still waits for the detailed study.

One more opportunity of using metal chelate gelatin-immobilized matrices is creation of ion-selective electrodes which, according to IUPAC definition, are sensors whose potentials linearly depend on the logarithm of activity of a determined ion in a solution. Ion-selective electrodes with solid, liquid and film membranes are known. In film membranes the same substances are active, for liquid membranes, but on a polymeric matrix, in particular polyvinylchloride. Gelatin is a hydrophilic polymer capable to be mixed with water with formation of quasi-homogeneous colloid solutions in any ratio; separate cells of its structure are capable to lock in various metal ions. That is why metal complex gelatin-immobilized matrices will be convenient for formation of electrode systems with rather wide assortment of ions determined. Moreover, gelatin is one possible building material of biological membranes which, in principle, may be used for imitation of diverse biochemical processes proceeding at a cellular level of living organisms. This provides an opportunity to use metal complex gelatin-immobilized matrices for manufacture of bio-specific, ion-selective electrodes allowing determination of inorganic as well as organic compounds.

The opportunities of metal complex gelatin-immobilized matrices as sensor controls for various chemical compounds which, in principle, can be used both in chemical and in physico-chemical methods of analysis, are significant. A special opportunity is matrix systems as ion-selective electrodes, as mentioned above. But their realization in kinetic methods of analysis is important. Application of the such methods in inorganic and analytical chemistry is often complicated because systems investigated are rather labile, and to fix a condition in any of them at a specific time during a chemical process in a liquid phase is usually impossible. The problem of creation of such conditions during the course of a chemical reaction at temperatures preferable for chemical processes in water (15–25°C) is difficult. Metal complex gelatin-immobilized matrix systems are unique objects with ability to fix and keep during a rather long time in the temperature interval indicated information. At the present time, however, this aspect of application of metal complex gelatin-immobilized matrix systems is elaborated in details only for research of complexation reactions.

As can be seen from all aforesaid, metal complex gelatin-immobilized matrices are useful in many areas of science and engineering; the above list is not exhaustive.

5. Conclusion

It follows from foregoing that complexation in the metal hexacyanoferrate(II) gelatin-immobilized matrix materials is important in chemistry as well as materials science. Despite the fact that an assortment of synthetic methods in coordination chemistry was elaborated (see, for example, [155, 247–252]), complexation in gelatin-immobilized matrices and in the metal hexacyanoferrate(II) ones, specifically, is an addition, allowing in some cases corresponding processes in milder conditions than with traditional ones in solution or solid phase. Up until now, however, it remains a little-known phenomenon for most specialists in the field of coordination chemistry and materials science, and, there is no information about synthetic or practical possibilities in authoritative books or reviews. No doubt in the future these possibilities will be manifested to a much greater extent.

Acknowledgement

The Foundation of Russian Foundation of Basic Researches (grant N 06-03-32003) is acknowledged for financial support.

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