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Complex formation processes in 3*d* metal hexacyanoferrate(II) gelatin-immobilised matrices

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Contents

I.	Introduction	657
II.	Metal hexacyanoferrate(II) gelatin-immobilised matrices	657
III.	Complex formation in the nickel(II) hexacyanoferrate matrix	661
IV.	Complex formation in the copper(II) hexacyanoferrate matrix	663
V.	Complex formation in cobalt(II) and cobalt(III) hexacyanoferrate matrices	666
VI.	Complex formation in the iron(III) hexacyanoferrate(II) matrix	668
VII.	Practical possibilities for complex formation reactions in metal hexacyanoferrate(II) matrices	669
VIII.	Conclusion	670

Abstract. Data on nontraditional complex formation reactions in iron(II, III), cobalt(II), cobalt(III), nickel(II), and copper(II) hexacyanoferrate(II) gelatin-immobilised matrices with fixation of the immobilised substances by intermolecular forces are surveyed and described systematically. Such reactions proceed when the matrices come into contact with aqueous solutions of nitrogen-, oxygen-, and sulfur-containing polydentate ligands. The practical possibilities for complex formation reactions in metal hexacyanoferrate(II) gelatin-immobilised matrices are demonstrated. The bibliography includes 147 references.

I. Introduction

Investigators in the field of coordination chemistry have shown in recent years an increased interest in metal–ion ligand systems in which the initial complex formation conditions differ significantly from those in solutions and in the solid phase. One of the most promising aspects is the study of complex formation in the so called metal-containing immobilised matrix systems where the initial chemical compounds and the products formed in the process are more or less rigidly fixed in the bulk of a polymer. Theoretically it is possible to represent two types of immobilisation of the substance: via the functional groups of the polymer or as a result of the operation of intermolecular forces.

In the former case, the corresponding polymers must contain structural fragments capable of binding the metal ions chemically to the polymer; the type of the metal–polymer bonds formed under these conditions (ionic, covalent, etc. bonds) is determined exclusively by the nature of the reactants.[1]

The second version presupposes a kind of 'fixation' of the immobilised substance as a result of dispersion, orientation, inductive, and other similar types of interaction. The 'fixation' requires only the presence of a large surface of the polymer. This type of immobilisation can be achieved via operations such as dispersion, adsorption, or precipitation of the substance in the polymer layer, sputtering, impregnation etc.[1]

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Naturally, there is also the possibility of an intermediate version where the 'fixation' as a result of the above types of interaction is accompanied also by the formation of fairly strong chemical bonds between the metal ions and the polymer molecules. The preparation of immobilised matrix systems of the first of the above types has promoted progress primarily in the field of metal complex catalysis; two parallel scientific fields began to develop simultaneously in this direction — immobilisation of coordination compounds on inorganic and organic bulk phase polymers.[1–5] Metal complex catalysis and organic synthetic reactions on polymer supports closely related to it[6–9] remain the main 'users' of the immobilised metal-containing matrix systems,[3] although to be fair one has to note that the range of their applications and their potential possibilities are much greater.[10–19] The extensive use of such systems has stimulated a series of specialised conferences during the last decade on problems of the synthesis and application of immobilised matrix systems.[20–23] The proceedings of these scientific forums constitute the contents of special issues of journals such as the *Journal of Molecular Catalysis* [**11**, 1, 2 (1981)] and the *British Polymer Journal* [**16**, 4 (1984)].

Analysis of the literature data makes it possible to claim that on the whole the immobilised matrix systems of the first type and the complex formation processes in them have by now been already fairly well investigated; at any rate, a whole series of monographs and review articles have been devoted to them and a list of these may be found, in particular, in Pomogailo's book.[1] On the other hand, complex formation in metal-containing immobilised matrices with fixation of the substance by intermolecular forces as well as the matrix systems themselves have not so far attracted any serious attention by investigators. The aim of the present review is to fill the existing gap to some extent.

II. Metal hexacyanoferrate(II) gelatin-immobilised matrices

The nature of both the polymer binder (which may influence significantly the selectivity of the complex formation reaction and the morphology of the reaction products) and of the immobilised chemical compound itself is of fundamental importance for the achievement and subsequent investigation of complex formation under the specific conditions created when chemical reactions take place in immobilised metal-containing matrices, where the substance is attached via intermolecular forces. The screening

which we carried out of natural and synthetic polymers in the immobilised substances showed that a low-molecular-mass polypeptide, namely gelatin, which is distinguished by the isotropic nature of its physicomechanical characteristics, transparency, hydrophilicity, and plasticity, is most suitable for the solution of the above problem. Among immobilised substances, preference should be given to 3*d* metal hexacyanoferrates(II) (MHCF), which successfully combine rigidity of attachment to the polymer, optimum kinetic lability, stability, and extremely low solubility in water.[24] Typical examples of such matrix systems are hexacyanoferrate(II) gelatin-immobilised matrices (MHCF-GIM), where iron(III), cobalt(II, III), nickel(II), and copper(II) hexacyanoferrates(II) are most often employed. In such matrices, the complex formation reactions take place as a result of the contact between the matrices and aqueous solutions of chelating ligands.[25]

1. Synthesis and structure

Despite its apparent simplicity, the synthesis of the MHCF-GIM is a specific and fairly laborious process.[24] Silver halide gelatin-immobilised matrices (AgHal-GIM), which are none other than the photosensitive emulsions in modern photographic materials, serve as a convenient starting material. Such matrices can be transformed fairly readily into silver-containing GIM, since the size of the silver particles is comparable to that of large clusters. For this purpose, one can employ the development and subsequent fixation processes well known in chemical photographic science and practice.[26-28] In its turn, it is possible to obtain from the silver-containing GIM, by means of specific chemical reactions, immobilised matrix systems with a very wide assortment of metal-containing compounds, retaining at the same time the quasi-molecular dispersity level of their particles which has been achieved for silver-containing GIM. The synthesis of the MHCF-GIM with iron(III), nickel(III), and copper(II) metal ions from the initial silver-containing GIM is carried out in two stages.[25,29-31]

In the first stage, the matrix is treated with a solution containing potassium hexacyanoferrate(III) and the oxalate, citrate, or tartrate complex of the corresponding 3*d* metal ion, as well as an agent for the establishment of the optimum pH in the precipitation of the target metal hexacyanoferrate(II). As a result, MHCF containing the given ion and silver(I) hexacyanoferrate(II) or other silver(I) compounds still less soluble in water, in particular AgCl or AgBr, are precipitated in the gelatin layer of the photographic material.

In the second stage, the GIM obtained are treated with an aqueous solution of sodium thiosulfate, as a result of which $Ag_4[Fe(CN)_6]$ or AgHal is transformed into the readily water-soluble compound $Na_3[Ag(S_2O_3)_2]$, which is removed from the bulk of the polymer to the solution. On decomposition of the polymeric binder in the resulting metal-containing GIM by protolytic enzymes, the complexes $KFe[Fe(CN)_6]$, $Ni_2[Fe(CN)_6]$, and $Cu_2[Fe(CN)_6]$ can be isolated from these matrices.[24] Bearing in mind the factors noted above as well as data on the compositions of the oxalate, citrate, and tartrate complexes of the corresponding 3*d* elements,[32-34] the transformation of the silver-containing GIM into the target iron(III), nickel(II), and copper(II) hexacyanoferrate(II)-GIM can be described with the aid of the following reactions[35]

$$\{2\,AgHal\} + HO\text{-}C_6H_4\text{-}OH + 2\,OH^- \longrightarrow \{2\,Ag\} + HO\text{-}C_6H_4\text{=O} + 2\,Hal^- + H_2O, \quad (1)$$

$$\{Ag + AgHal\} + 2S_2SO_3^{2-} \longrightarrow \{Ag\} + Ag(S_2O_3)_2]^{3-} + Hal^-, \quad (2)$$

$$2Fe_2(HCt)(HTr) + 4\{Ag\} + 4[Fe(CN)_6]^{3-} + 3K^+ \longrightarrow \{3KFe[Fe(CN)_6] + Ag_4[Fe(CN)_6]\} + 2HCt^{3-} + [Fe(HTr)_2]^{3-}, \quad (3)$$

$$\{3KFe[Fe(CN)_6] + Ag_4[Fe(CN)_6]\} + 8S_2O_3^{2-} \longrightarrow \{3KFe[Fe(CN)_6]\} + 4[Ag(S_2O_3)_2]^{3-} + [Fe(CN)_6]^{4-}, \quad (4)$$

$$6[Ni(HCt)_3]^{7-} + \{Ag\} + 4[Fe(CN)_6]^{3-} + 4Cl^- \longrightarrow \{3Ni_2[Fe(CN)_6] + 4AgCl\} + [Fe(CN)_6]^{4-} + 18HCt^{3-}, \quad (5)$$

$$\{3Ni_2[Fe(CN)_6] + 4AgCl\} + 8S_2O_3^{3-} \longrightarrow \{3Ni_2[Fe(CN)_6]\} + 4Ag(S_2O_3)_2]^{3-} + 4Cl^-, \quad (6)$$

$$6[Cu(Ox)_2]^{2-} + 4\{Ag\} + 4[Fe(CN)_6]^{2-} \longrightarrow \{3Cu_2[Fe(CN)_6] + Ag_4[Fe(CN)_6]\} + 12Ox^{2-}, \quad (7)$$

$$\{3Cu_2[Fe(CN)_6] + Ag_4[Fe(CN)_6]\} + 8S_2O_3^{2-} \longrightarrow \{3Cu_2[Fe(CN)_6]\} + 4[Ag(S_2O_3)_2]^{3-} + [Fe(CN)_6]^{4-}, \quad (8)$$

where H_2Ox, H_4Ct, and H_4Tr are oxalic, citric, and tartaric acids respectively, the immobilised chemical compounds being indicated in braces.

The synthesis of the cobalt(II) hexacyanoferrate(II)-GIM is more complex and includes three stages:[35-37]

$$4\{Ag\} + 4[Fe(CN)_6]^{3-} \longrightarrow \{Ag_4[Fe(CN)_6]\} + 3[Fe(CN)_6]^{4-}, \quad (9)$$

$$\{Ag_4[Fe(CN)_6]\} + 2CoCl_2 \longrightarrow \{Co_2[Fe(CN)_6] + 4AgCl\}, \quad (10)$$

$$\{Co_2[Fe(CN)_6] + 4AgCl\} + 8S_2O_3^{2-} \longrightarrow \{Co_2[Fe(CN)_6]\} + 4[Ag(S_2O_3)_2]^{3-} + 4Cl^-. \quad (11)$$

As regards cobalt(III) hexacyanoferrate(II) matrices, the nature of the immobilised substance contained in them still cannot be regarded as finally established. It has been suggested that the compound present in the GIM is the simple cobalt(III) hexacyanoferrate(II) $Co_4[Fe(CN)_6]_3$,[24,35,38] but the latest data indicate that $KCo[Fe(CN)_6]$ should be regarded as a more probable compound. This compound is diamagnetic,[24] which indicates the presence in the latter of Fe(II) and Co(III) ions in an octahedral environment of CN-ligands with O_h symmetry. This complex should be considered as a kind of intermediate between $KCo^{III}[Fe^{II}(CN)_6]$ and $KFe^{II}[Co^{III}(CN)_6]$. Like the $KFe[Fe(CN)_6]$, $Ni_2[Fe(CN)_6]$ or $Cu_2[Fe(CN)_6]$-GIM, the KCo.[Fe(CN)$_6$]-containing GIM may be synthesised from silver-containing gelatin-immobilised matrices in a two-stage treatment in accordance with the equations

$$3[Co(HCt)_2]^{3-} + 4\{Ag\} + 4[Fe(CN)_6]^{3-} + 4Cl^- + 3K^+ \longrightarrow \{3KCo[Fe(CN)_6] + 4AgCl\} + 6HCt^{3-} + [Fe(CN)_6]^{4-}, \quad (12)$$

$$\{3KCo[Fe(CN)_6] + 4AgCl\} + 8S_2O_3^{2-} \longrightarrow \{3KCo[Fe(CN)_6]\} + 4[Ag(S_2O_3)_2]^{3-} + 4Cl^-. \quad (13)$$

The technological processes involving the preparation of the target MHCF-GIM and the compositions of the solutions with which the system was treated in each of the stages have been described in detail.[39-84]

It is known that, in terms of its chemical nature, gelatin is a polydisperse mixture of low-molecular-mass polypeptides ($M = 50\,000 - 70\,000$) and their aggregates ($M = 200\,000 - 300\,000$).[27,28,85,86] According to the literature,[87,88] gelatin molecules consist of three α-type polypeptide chains with almost identical molecular masses, two α-chains being usually almost identical as regards the set and sequence of the aminoacids (α1-chains), while the third (the α2-chain) differs in this respect from the other two. A structure has been proposed for such molecules,[89,90] in which a left-handed helical structure of the α-type was attributed to each polypeptide chain. Within the framework of such a structure, all three helices are 'plaited' with one another to form a single 'right-handed' helix, hydrogen bonds playing a significant role in the stabilisation, as was to be expected.[87] The α2-chains are characterised 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, isoleucine, histidine, and hydroxylysine.[28]

The sequence of the peptide fragments in the α1-chains with more than 700 aminoacid residues has now been fully elucidated.[27,28] It is of interest that, in contrast to other proteins, where no common features in the alternation of the aminoacids in the peptide fragments have been found, in gelatin, starting with the 17th residue, glycine invariably occupies each third position, so that the overall formula of the polypeptide units in the α1-chain can be written in the form Gly–X–Y, where Gly = glycine, while X and Y are other aminoacid residues. The glycine – proline – hydroxyproline combination is most frequently encountered.[27] The sequence of the aminoacid residues in the α2-chain has still not been accurately established.[28]

Like other proteins, gelatin is an ampholyte because it includes 'free' acid and basic groups (i.e. groups which can be titrated in aqueous solution) such as the β-carboxy-group of aspartic acid, the β-carboxy-group of glutamic acid, the β-imidazolyl group of histidine, the ε-amino-group of lysine, the δ-guanidino-group of arginine, and the phenolic hydroxy-group of tyrosine.[27,28] Their nitrogen and oxygen atoms can play the role of donor centres in relation to various *d* element ions, but, overall, gelatin is a fairly weak complex-forming agent.[27,28]

The present author's electron microscope studies of the MHCF-GIM classified above have shown that all these matrices are transparent to the electron flux and hence the particles of the immobilised MHCF attain a quasi-molecular level of dispersity. They can therefore be regarded as coordination polymers with a relatively low molecular mass and a fairly regular structure, being located in the cavities between the polypeptide units of the gelatin molecules.[35] Such polymers have a face-centred lattice with the *Fm*3 or the *Fm*3*m* symmetry space group and unit cell dimensions of 9.93 Å (Co), 10.18 Å (Ni), and 10.03 Å (Cu).[91] The coordination number (C. N.) of Fe(II) is 6 and an octahedral envirnonment comprising the CN-groups is characteristic of this ion. The ions of the other 3*d* element in the MHCF have coordination numbers of 4 and 6 (tetrahedral and octahedral environments).

Quantum-chemical calculations for the CN^- ions have shown that the electron density on the carbon atom is almost three times greater than on the nitrogen atom,[92] so that the carbon atom is a harder donor centre than nitrogen. Since Fe(II) is a harder Pearson acid than Co(II), Ni(II), and Cu(II) (their orbital electronegativities in solution are +0.69, +0.52, +0.29, and −0.55 eV respectively)[93] and exhibit a lower affinity for nitrogen, the Fe–CN–M (M = Co, Ni, Cu) structural fragments are formed. Similar group of atoms arise also in the complex KCo[Fe(CN)] or $Co_4[Fe(CN)]_3$ because the affinity of Co(III) for nitrogen is much higher than that of Fe(II), while the affinity of Fe(II) for carbon greatly exceeds the affinity of Co(III) for this element. Some of the iron atoms in KFe[Fe(CN)] are coordinated via the carbon atom, whilst others are coordinated via the nitrogen atom, so that the Fe–CN–Fe groups are produced.[91] Thus, in all the MHCF coordination polymers considered here, iron is coordinated to the cyano-group via the carbon atom, whilst all other *d* elements are coordinated via the nitrogen atom.[92]

The elastic properties of bulk-phase gelatin resemble those of rubber; this is quite natural for infinite chains formed by long chains of molecules connected by a limited number of cross links.[94] This structure is potentially suitable for the formation of polymer-immobilised matrices because it does not permit the formation of any kind of rigid crystalline blocks and furthermore contains a fairly large number of cells for the reception and subsequent fixation of the molecules of the immobilised substance. When filled with the molecules of the corresponding chemical compund, these cells retain a certain freedom of migration in space. With a polymer of such a structure it is possible, in principle, to obtain immobilised matrices characterised by a fairly uniform distribution of the metal-containing substance in some part of the bulk-phase polymer. Furthermore, such matrices are sterically accessible for the occurrence of diverse chemical processes, in particular complex formation. Gelatin has an extremely high surface area and an extensive system of micropores, so that when it comes into contact with any kind of aqueous solution the permeation of both the solvent molecules and of the solute into the bulk-phase polymer is as a rule ensured comparatively readily.[27,28]

2. Specific features of the complex formation reactions

Taking into account the entire set of data concerning gelatin as a polymeric material and also the topography of the immobilised matrix system obtained on its basis, one can discern the following features of complex formation reactions occurring in these systems:[24,35] hindered contacts between the reactants; the presence of a charge on the polymer molecules in contact with the ligand solution because gelatin is an ampholyte; an extremely small reaction volume in which the complex formation process takes place; limited mobility of the complex-forming agent [i.e. of the immobilised metal hexacyanoferrate(II)]; a low rate of 'supply' of the ligand to the bulk-phase polymer; the nonequilibrium nature of the complex formation process.

The above factors make it possible to predict the preferential formation and accumulation in the GIM of the following coordination compounds which are not characteristic of complex formation in solution and in the solid phase:[24,35] intermediate complex forms, ligand-deficient complexes, coordination dimers and polymers, and chelates with a pronounced deficiency of protons. Complex formation in MHCF-GIM systems should therefore be regarded as a completely specific phenomenon in coordination chemistry, requiring for its description a model different from that of complex formation in solution and in the solid phase.

The methodological foundations of such a model have been considered.[95] Although all the MHCF-GIM – aqueous chelating ligand solution systems are typically heterogeneous, complex formation reactions in them can be regarded, to a satisfactory approximation, as quasi-homogeneous because they take place not at the solid – liquid (matrix – ligand solution) interface but in the bulk phase of the polymer.

The point is that, according to electron microscope data, the hexacyanoferrate(II) in the MHCF-GIM is present in the massive gelatin in the form of a layer 10–20 μm thick, above which there is a layer of gelatin with a thickness ranging from 2 to 15 μm.[35] On this basis, the MHCF-GIM can be regarded as the reaction microvolume present in the solid phase and in contact with the aqueous ligand solution, on the one hand, and as a kind of intermediate state between the solution and the solid phase, on the other. When this matrix comes into contact with an aqueous ligand solution capable of forming with the ion of the metal M

thermodynamically more stable coordination compounds of the hexacyanoferrate complex, the ligand, diffusing in the massive polymer, reacts with M and binds it in the corresponding chelate complex. On the other hand, the iron(II) in the metal hexacyanoferrate(II) coordination polymer is transformed into the kinetically extremely inert and thermodynamically stable anion $[Fe(CN)]^{4-}$, which passes from the MHCF-GIM to the solution in contact with it.

When Fe–CN–M (M = Fe, Co, Ni, Cu) groups are attacked by an alkaline solution of the ligand, their fate is determined by the ratio of the M–N and M–O bond energies. One may predict that, for $E_{M-N} > E_{M-O}$, the metal hexacyanoferrate(II) will prove resistant to the action of the OH^- ions present in the alkaline solutions of the ligands and will enter into a direct interaction with the corresponding ligand. For $E_{M-N} < E_{M-O}$, the M–N bonds will initially dissociate and will be replaced by the M–O bonds, so that the metal ion–ligand interaction in the MHCF-GIM will be preceded by the decomposition of the hexacyanoferrate(II) by the OH^- ions, which will be accompanied by the formation of coordination polymers of the corresponding oxides, oxide hydroxides, and hydroxides with O or OH bridging groups.[24] The version with $E_{M-N} > E_{M-O}$ occurs in the case of the $Ni_2[Fe(CN)]$ and $KCo[Fe(CN)]$ matrices, while that with $E_{M-N} < E_{M-O}$ occurs in the case of $KFe[Fe(CN)]$, $Co_2[Fe(CN)]$, and $Cu_2[Fe(CN)]$ matrices.

It may be expected that, in the first two matrices, interaction between the hexacyanoferrates(II) of the 3*d* elements and moderately soft and soft Pearson bases (the nitrogen-, nitrogen- and oxygen-, and nitrogen-containing ligands considered below are in fact of this kind) is accompanied by the dissociation of the M–NC bonds and the formation of stronger bonds between the metal and the donor centres of the ligand, the Fe–CN bonds being retained under these conditions. When the coordination number of Fe(II) in the structures of the hexacyanoferrates(II) of 3*d* elements is 6, there is no steric hindrance to the formation of the very stable inert anion $[Fe(CN)]^{4-}$ of configuration $t_{2g}(\pi^2_{d_{xy}}\pi^2_{d_{xz}}\pi^2_{d_{yz}})$ and ligand field stabilisation energy (LFSE) equal to $+24D_q$.[91,96] However, in the case of matrix systems with $KFe[Fe(CN)]$, $Co_2[Fe(CN)]$, and $Cu_2[Fe(CN)]$, the hexacyanoferrates(II) interact with the OH^- ion, the process being accompanied by dissociation of M–NC bonds and formation of M–O bonds with retention of the Fe–CN bonds and hence the formation of the anion $[Fe(CN)]^{4-}$.[24,91]

Special studies by the present author showed that gelatin does not interact with any of the (N, O)-, (N, S)-, (O, S)-, and (S, S)-ligands or with any of the hexacyanoferrates(II) of 3*d* elements.[24,35,95,97,98] Furthermore, the complex formation products diffusing from the matrix to the solution also do not interact with any of these ligands or with gelatin. One can therefore claim that the solid–solution interface should not influence complex formation processes occurring in the GIM.[95] Previously it was mentioned that the substance contained in the MHCF-GIM is not located on the surface of the matrix and is not dispersed uniformly throughout the massive polymer, but is, as it were, 'imbedded' at a certain depth. This factor and also the inertness of gelatin to the ligands suggests that the ligand diffusion process is not accompanied by a chemical reaction over the entire path traversed and that the MHCF–ligand interaction occurs only after the ligand 'diffusion path' has been traversed. It has therefore been suggested that complex formation in the MHCF–GIM systems be described in terms of the mathematical procedures of the so called external problem of diffusion kinetics.[24,95,99]

3. Kinetic aspects of the complex formation

The complex formation process in the MHCF–GIM systems can occur theoretically either via an associative mechanism (S_N2) or via a pseudo-dissociative mechanism (S_N1).[24,25,35,95] In the former case, the MHCF is stable towards OH^- ions and the ligand molecules therefore gradually enter the inner sphere of the MHCF coordination polymer and $[Fe(CN)]^{4-}$ is then eliminated; this version occurs on complex formation in the $KCo[Fe(CN)]$–GIM [25,38] and $Ni_2[Fe(CN)]$–GIM [25,30,96,97] systems. The rate of complex formation is governed by a bimolecular reaction. In the second case, the MHCF present in the matrix undergoes alkaline degradation by the OH^- ions to the corresponding oxide or oxide hydroxide, which are involved in the subsequent reaction between the metal ion and the ligand.

On the one hand, the rate of formation of the oxide or hydroxide depends on the MHCF concentration in the matrix but is independent of the ligand concentration in solution and this reflects the clear analogy with typical dissociative processes. On the other hand, the rate of complex formation proper is in this case also limited by a bimolecular reaction. The mechanism of this version of complex formation in the MHCF–GIM has in fact been referred to as of the 'pseudo-S_N1' type;[25,31] it operates in complex formation reactions in the $KFe[Fe(CN)]$–GIM [25,29,70] and $Cu_2[Fe(CN)]$–GIM [25,32,76] systems and partly in the $Co_2[Fe(CN)]$–GIM.[37]

The model of complex formation in the MHCF–GIM which combines the mathematical procedures of the external diffusion kinetic problem with the kinetic equations within the framework of the Guldberg–Waage law has been used to analyse the experimental relations

$$D' = f(c_F,\ c_L^0,\ t),$$

where D' is the optical density of the metal chelate GIM, c_F the molar concentration of the MHCF in the matrix, c_L^0 the molar concentration of the ligand in solution, and t the duration of the complex formation reaction.

In the case of an associative mechanism, the set of proposed computational equations is

$$\lg\left(c_F\frac{d\alpha}{dt}\right) = \lg k_1 + m\lg c_F(1-\alpha) + l\lg c_L^0 + l\lg\left[1-\exp\left(-\frac{\Delta t}{Mh^2}\right)\right], \quad (14)$$

$$\lg\left(c_F\frac{d\beta}{dt}\right) = \lg k_2 + p\lg c_F(\alpha-\beta) + q\lg c_L^0 + q\lg\left[1-\exp\left(-\frac{\Delta t}{Mh^2}\right)\right], \quad (15)$$

$$\lg\left(c_F\frac{d\omega}{dt}\right) = \lg k_i + y\lg c_F(\psi-\omega) + z\lg c_L^0 + z\lg\left[1-\exp\left(-\frac{\Delta t}{Mh^2}\right)\right]. \quad (1)$$

The following set of equations correspond to a dissociative mechanism:

$$\lg\left(c_F\frac{d\alpha'}{dt}\right) = \lg k_{OH} + m'\lg c_F(1-\alpha') + l'\lg c_L^0 + l'\lg\left[1-\exp\left(-\frac{\delta t}{Mh^2}\right)\right], \quad (17)$$

$$\lg\left(c_F\frac{d\beta'}{dt}\right) = \lg k_1 + p'\lg c_F(\alpha'-\beta') + q'\lg c_L^0 + q'\lg\left[1-\exp\left(-\frac{\Delta t}{Mh^2}\right)\right], \quad (18)$$

$$\lg\left(c_F\frac{d\omega'}{dt}\right) = \lg k_j + y'\lg c_F(\psi'-\omega') + z'\lg c_L^0 + z'\lg\left[1-\exp\left(-\frac{\Delta t}{Mh^2}\right)\right]. \quad (19)$$

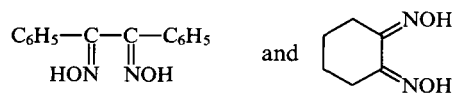
In these equations, k_1, k_2, k_i, and k_j are the rate constants for the consecutive complex formation stages, k_{OH} is the rate constant for the alkaline degradation of the MHCF, *m*, *l*, *p*, *q*, *y*, *z*, *m'*, *l'*, *p'*, *q'*, *y'*, and *z'* are the stoichiometric coefficients in the equations for the complex formation reactions, α' is the degree of accumulation of the hydroxide (or oxide hydroxide) of the corresponding metal ion in the GIM, α, β, ψ, ω, β', ψ', and ω' are the degrees of accumulation of various complexes in the matrix, Δ and δ are the diffusion coefficients of the ligand molecules and OH^- ions for diffusion from the solution to the bulk-phase polymer respectively, *M* is the molecular mass of the ligand, and *h* is the length of the 'diffusion path' traversed by the ligand from the surface of the matrix to the surface of the layer of the MHCF present in it.[35] A program for the computer-mathematical treatment of the experimental relations $D' = f(c_F, c_L^0, t)$ has been compiled with the aid of these equations. It made it possible to calculate the stoichiometric coefficients in the equations for the elementary steps and the overall complex formation processes for a whole series of MHCF – (N), (O), (S), (P)-ligand systems. The theoretical aspects of the kinetics of the complex formation reactions in the MHCF – GIM have been studied in detail.[24,95]

III. Complex formation in the nickel(II) hexacyanoferrate matrix

1. Complex formation in the Ni(II) – (N, O)-ligand systems

According to the available data,[100-105] nickel(II) forms a fairly large number of sparingly soluble chelate complexes with various (N, O)-ligands. Despite this, there are only isolated instances of their employment for complex formation in the $Ni_2[Fe(CN)_6]$ – GIM. The Ni(II)-dimethylglyoxime system has been indisputably characterised in greatest detail among the systems considered.

The study of complex formation in a MHCF – GIM system was first reported by Mikhailov and Polovnyak.[40] The results of their study as well as those of later and detailed investigations[24,35,77] indicate the formation in this system of four different dimethylglyoximate complexes, namely $Ni(HL)_2$ (purple), $NiL(H_2O)_2$ (carmine red), $[Ni(H_2L)]Cl_2$ (yellow-green), and $[Ni(H_2L)_2]Cl_2$ (blue) (H_2L = dimethylglyoxime). In two other systems, containing ligands related to dimethylglyoxime, namely benzil glyoxime [diphenylglyoxime] and nioxime [1,2-cyclohexanedione dioxime]

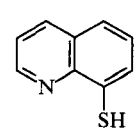


the complex formation processes proceed in approximately the same way as in the Ni(II) – dimethylglyoxime system, as was to be expected. However, the number of coordination compounds formed in this process {$Ni(HL)_2$ and $[Ni(H_2L)_2]Cl_2$} is smaller than in the Ni(II) – dimethylglyoxime system.[24]

The formation of only one complex NiL_2 (L^- = deprotonated form of the ligand) has been detected in the Ni(II) – 1-nitroso-2-naphthol, Ni(II) – 2-nitroso-1-naphthol, Ni(II)-8-hydroxyquinoline, and Ni(II) – 8-hydroxy-5-methylquinoline systems.[24] It is remarkable that the nature of the complex formation in all the systems enumerated remains virtually the same both in aqueous solutions and in the solid phase; the number and compositions of the complex species formed in both cases are the same.[35]

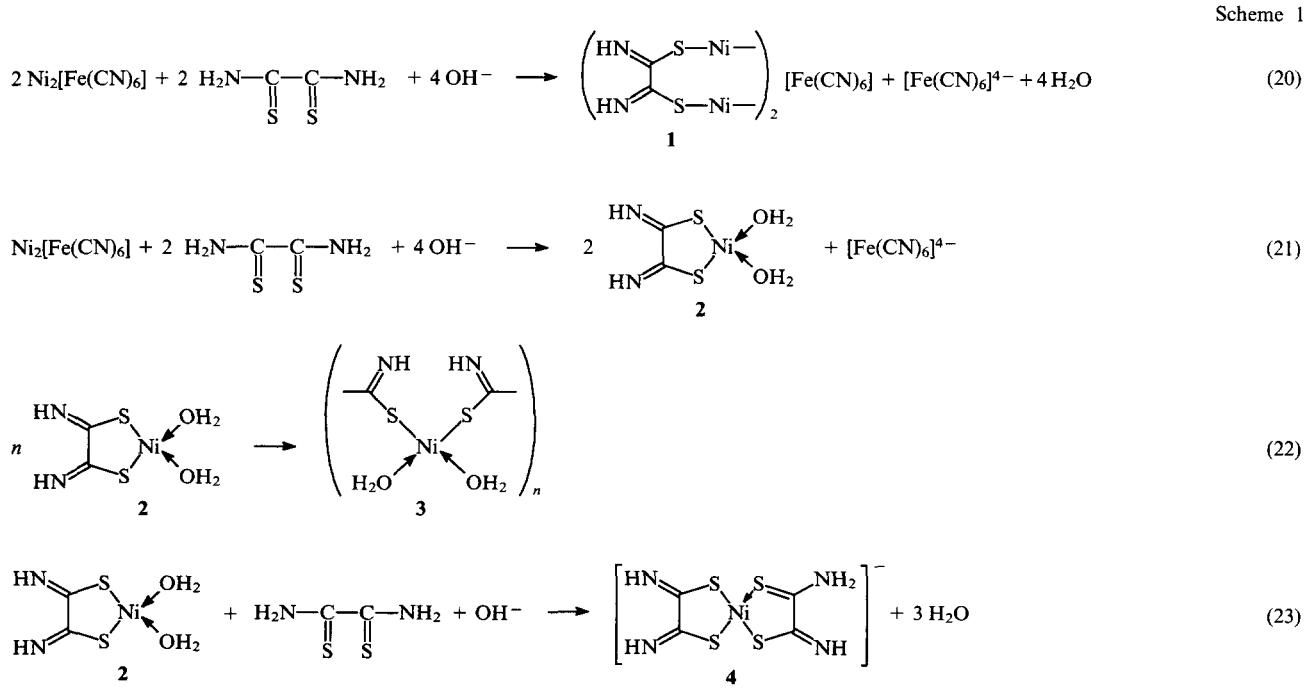
2. Complex formation in the Ni(II) – (N, S)-, (O, S)-, (S, S)-ligand systems

The rule governing the formation of the Ni(II) – ligand complexes in the $Ni_2[Fe(CN)_6]$ – GIM system noted above holds also when any kind of (N, S)-, (O, S)-, or (S, S)-ligand capable of giving rise to only one deprotonated species in aqueous solution participates in this process.[24,35] As an example, one may quote 8-mercaptoquinoline



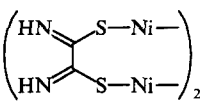
and its alkyl, aryl, and halo-derivatives. A number of studies have been devoted to the formation of complexes in the $Ni_2[Fe(CN)_6]$ – GIM with participation of such ligands.[25,30,60,68,74,81] Only coordination compounds having the composition NiL_2, where L^- = singly deprotonated ligands, are formed in the Ni(II) – 8-mercaptoquinoline system, exactly as in the systems Ni(II) – alkyl, aryl, and halo-derivatives of 8-mercaptoquinoline (in particular 2-methyl, 5-methyl, 2,7-dimethyl-, 2,4,6-trimethyl-, 5-phenyl-, 6-phenyl-, 5-bromo-, and 5-methylthio-8-mercaptoquinoline) at pH > 9.

Scheme 1



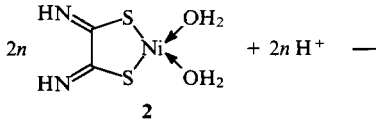
The conclusion reached in the studies quoted above concerning the number and composition of the complex species formed agrees completely with data for complex formation with the 8-mercaptoquinolines listed above in solution and in the solid phase. These are presented in a monograph[106] and in later communications, in particular in Refs 107–109. However, the situation changes significantly when the (N, S)-ligand is capable of forming several species with different degrees of deprotonation, for example HL^- and L^{2-}.[35] In conformity with the prediction made above, in this case ligand- and proton-deficient metal chelates do indeed arise on complex formation in the $Ni_2[Fe(CN)_6]$ matrix. Incidentally many of them have still not been detected in the corresponding Ni(II)–(N, S)-, (O, S)-, (S, S)-donor atom ligand systems in solution and in the solid phase.

The formation of the complex



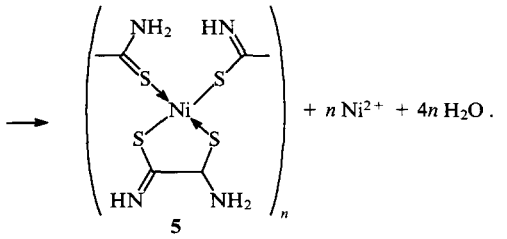
in the $Ni_2[Fe(CN)_6]$–GIM system, considered in detail in a number of investigations,[25,30,40,58,66,69,71,97] constitutes the most striking example. Analysis of relations of the type $D' = f(c_F, c_L^0, t)$ in various coordination regimes in the Ni(II)–dithiooxamide system[25,30,97] shows that the anions $[Fe(CN)_6]^{4-}$ are gradually eliminated from the inner sphere of the $Ni_2[Fe(CN)_6]$-coordinated polymers during complex formation, the process being accompanied by an increase in c_L^0 in accordance with the S_N2 mechanism. The ligand-deficient complex $(Ni_2L)_2[Fe(CN)_6]$ (grey-blue) **1**, the monomeric (complex **2**), the polymeric (complex **3**) proton-deficient complexes $NiL(H_2O)_2$ **2** (pink-violet) and $[NiL(H_2O)_2]_n$ **3** (violet), and a soluble complex having the probable composition $[Ni(L)HL]^-$ **4** with the ratio Ni(II) ion : ligand = 1 : 2, where H_2L = dithiooxamide, are formed in succession under these conditions. According to literature data,[30,97,110] their formation in the GIM can be represented with the aid of Scheme 1 (see previous page).

It is striking that the monomeric chelate is rapidly and irreversibly transformed at pH<5 into the coordination polymer $[Ni(HL)_2]_n$ (dark blue)[30,97,110] in accordance with the scheme



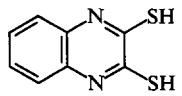
(24)

2



5

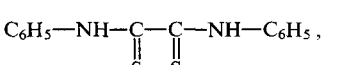
Thus, in the formation of the Ni(II)–dithiooxamide complexes in the $Ni_2[Fe(CN)_6]$–GIM system, at least five different coordination compounds arise, whereas in solution only one complex, namely $[Ni(HL)_2]_n$, is produced.[111–119] The diversity of coordination compounds arising during complex formation in the Ni(II)–quinoxaline-2,3-dithiol system is somewhat smaller.



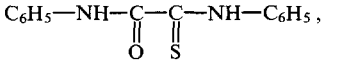
Quinoxaline-2,3-dithiol can be regarded as a rigidly structured analogue of dithiooxamide, which is invariably coordinated to Ni(II) via two sulfur atoms.

According to the results of the mathematical analysis of the $D' = f(c_F, c_L^0, t)$ curves and the chemical analysis of the compounds isolated from the corresponding metal chelate GIM, the complexes $(Ni_2L)_2[Fe(CN)_6]$ (orange), $NiL(H_2O)_2$ (pink), and the soluble complex $[NiLHL]^-$ are formed in succession with increase in c_L^0 in the Ni(II)–quinoxaline-2,3-dithiol system, as in the Ni(II)–dithiooxamide system.[30,69,120,121] Like the monomeric chelate $NiL(H_2O)_2$ with dithiooxamide, the chelate $NiL(H_2O)_2$ with quinoxaline-2,3-dithiol is readily transformed at pH < 5 into a 1 : 2 chelate with a singly deprotonated ligand. However, in contrast to the Ni(II)–dithiooxamide system, in this case the conversion of complex **2** into complex **5** is reversible and at pH > 9 the chelate **5** is converted reversibly into $NiL(H_2O)_2$. According to the literature data,[25,30,120] this difference is associated with the fact that the 1 : 2 complex with the HL^- form of quinoxaline-2,3-dithiol is a monomer whereas the chelate, having a similar composition, with the HL^- form of dithiooxamide is a coordination polymer. The formation of the polymeric chelate $[Ni(HL)_2]_n$ with quinoxaline-2,3-dithiol is sterically hindered because the ligand is cumbersome; for the same reason, quinoxaline-2,3-dithiol does not form with Ni(II) the coordination polymer $[NiL(H_2O)_2]_n$ either.[25,35] On the other hand, data[122,127] concerning complex formation in the Ni(II)–quinoxaline-2,3-dithiol system in solution indicate unambiguously the formation of only one coordination compound, namely $Ni(HL)_2$.

All that has been said about the Ni(II)–dithiooxamide and Ni(II)–quinoxaline-2,3-dithiol systems permits the conclusion that, with the aid of complex formation processes in the $Ni_2[Fe(CN)_6]$–GIM systems, it is indeed possible to synthesise many more coordination compounds than in solution or in the solid phase. On the other hand, the complex formation process in the system containing Ni(II) and another cumbersome structural analogue of dithiooxamide, namely *N,N'*-diphenyldithiooxamide



results in the formation of only one coordination compound — $Ni(HL)_2$, as in complex formation in solutions.[69,71,98,128] However, when another ligand, namely *N,N'*-diphenylthiooxamide



which differs from the preceding one only by the fact that one of its sulfur atoms has been replaced by an oxygen atom, is used in the complex formation process in the nickel(II) hexacyanoferrate(II)–GIM, a much greater number of coordination compounds (namely four) can again be obtained than on complex formation in solution or in the solid phase (one complex).[78,98]

The causes of such a sharp difference in the nature of complex formation in the Ni(II)–(N, O)-ligand and the Ni(II)–(N, S)-, (O, S)-, or (S, S)-ligand systems in the $Ni_2[Fe(CN)_6]$–GIM have been considered.[24,98] The small tendency of the Ni(II) chelates with the HL^- forms of the (N, S)-, (O, S)-, and (S, S)-ligands to split off protons even at high

pH (13 and above) and the fact that (N, S)-, (O, S)-, and (S, S)-ligands of the type H_2L, the proton-donating capacity of which is usually much smaller compared with their (N, O)-analogues even in a highly alkaline medium, generate insufficient amounts of the L^{2-} forms of the ligands for the formation of complexes with Ni(II) were specified as the most important causes. The deficiency of the L^{2-} form prevents the formation of the Ni(II) chelates with this species on complex formation in solution.

However, the migration of some of the protons from the inner coordination sphere of the Ni(II) chelates with the HL^- forms of the (N, S)-, (O, S)-, and (S, S)-ligands and their binding by the negatively charged gelatin molecules become possible on complex formation in the $Ni_2[Fe(CN)_6]$-GIM system where the molecules of the massive polymers have a negative charge (see Section II, 2).

By virtue of this factor, the possibility of the formation of metal chelates with a pronounced deficiency of protons, which is ruled out in solution and in the solid phase, appears on complex formation in the $Ni_2[Fe(CN)_6]$-GIM system. On the other hand, in the case of the (N, O)-donor atom ligands of the type H_2L, the ligands themselves are capable of generating sufficient amounts of the L^{2-} species for the formation of Ni(II) complexes in a highly alkaline solution. This ensures the possibility of formation in solution of chelates both with the HL^- and L^{2-} species. Therefore in the case of the (N, O)-ligands the formation of any new complex species, which would not be detected on complex formation in the Ni(II)-(N, O)-donor atom ligand systems in solution, is not observed in the $Ni_2[Fe(CN)_6]$-GIM system.[24,77] Thus the study of the complex formation processes in the $Ni_2[Fe(CN)_6]$-GIM has fully confirmed the prediction that ligand-deficient complexes, coordination polymers, and chelates with a pronounced proton deficiency may be formed under these specific conditions.[25,30,97,98,111]

IV. Complex formation in the copper(II) hexacyanoferrate matrix

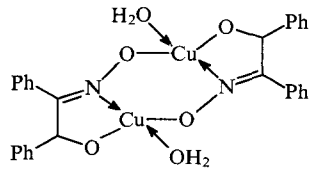
1. Complex formation in the Cu(II)-(N, O)-ligand systems

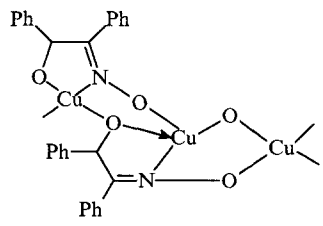
Like Ni(II), Cu(II) belongs to the class of fairly soft Pearson acids.[129] Nevertheless Cu(II) forms an extremely large number of chelate complexes with organic ligands, the donor centres of which are the 'hard' nitrogen and oxygen atoms, in particular with complexones,[96,100,130-132] oximes,[104] 8-hydroxyquinoline, nitrosonaphthols and their substituted derivatives,[105] and Schiff bases.[96,100] Therefore comparison of the possibilities for the formation of Ni(II) and Cu(II) complexes with (N,O)-ligands in the corresponding MHCF-GIM systems is particularly interesting because in the case of the $Ni_2[Fe(CN)_6]$-GIM system the process proceeds via an associative S_N2 mechanism,[25,30] while in the case of the $Cu_2[Fe(CN)_6]$-GIM system it proceeds via a pseudo-dissociative S_N1 mechanism.[25,31] The available literature data on this subject, in particular data concerning the formation of complexes in the Cu(II)-8-hydroxyquinoline, Cu(II)-8-hydroxy-2-methylquinoline, Cu(II)-8-hydroxy-2-methylquinoline,[24,35] and Cu(II)-α-benzoin oxime[24,35,80] systems in the $Cu_2[Fe(CN)_6]$-GIM show that the alkaline degradation of copper(II) hexacyanoferrate(II) take place initially in all cases with its transformation in the first stage into polymeric copper(II) hydroxo-complexes and ultimately into the polymeric hydroxide $[Cu(OH)_2]_n$.

$$\{Cu_2[Fe(CN)_6]\}_n + 2m\,OH^- \longrightarrow \longrightarrow 2[Cu_n(OH)_m]^{(2n+m)+} + n[Fe(CN)_6]^{4-}, \quad (25)$$

$$[Cu_n(OH)_m]^{(2n+m)+} + (2m-n)\,OH^- \longrightarrow [Cu(OH)_2]_n \quad (2)$$

The polymeric copper hydroxide formed as a result of these processes becomes a kind of 'starting area' for the subsequent interaction of copper(II) with the (N, O)-ligands indicated above, which causes the latter to enter the coordination sphere of Cu(II). The validity of processes (25) and (26) is indicated by the results of the mathematical analysis of the corresponding $D' = f(c_F, c_L^0, t)$ kinetic curves in the Cu(II)-(N,O)-ligand systems indicated, according to which for $t < 1$ min the chemical process proceeds without the attachment of ligand molecules to copper(II) ions over the entire range of c_F and c_L^0 investigated. Furthermore, the results of chemical analysis indicate unambiguously that, for $c_L^0 < 10^{-5}$ M and $t < 10$ min, only the polymeric hydroxo-complex $[Cu(OH)_2]_n$ is formed in all these systems in the GIM.[24,35] The clear predominance of the process involving the formation of copper(II) complexes with the ligands compared with the alkaline degradation of the $Cu_2[Fe(CN)_6]$-GIM has been noted only for $c_F < 1.0$ M, $c_L^0 > 1.0 \times 10^{-2}$ M, and $t >$ min.[24,35] In all the Cu(II) systems considered with 8-hydroxyquinoline and its derivatives, it has been possible to establish reliably the existence of only one complex species—CuL_2 (L^- is the deprotonated form of the ligand). In the Cu(II)-α-benzoin oxime system, only one coordination compound is also formed in the $Cu_2[Fe(CN)_6]$-GIM. Judging from the results of elemental analysis, the compound has an empirical formula close to CuL, where L^{2-} is the doubly deprotonated form of the ligand. Either a dimeric structure with two five-membered and one six-membered metallocycles and two coordinated water molecules[80] or a polymeric structure with a three-dimensional macrostructure, incorporating five-membered rings without coordinated water molecules,[24] may be attributed to the compound.





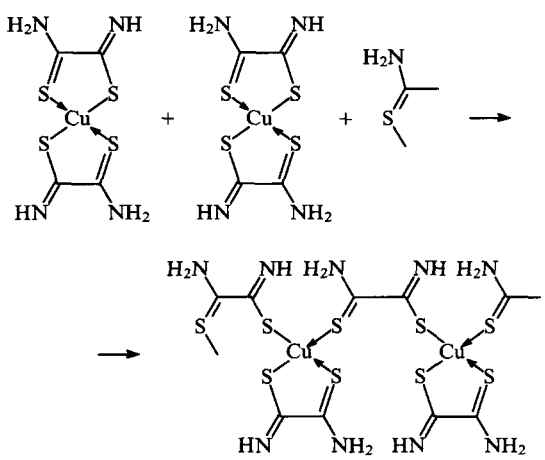
An unambiguous choice between them on the basis of the results of physical research methods is so far impossible. It is remarkable that the ligand in the system inhibits fairly appreciably the alkaline degradation of copper(II) hexacyanoferrate(II).[24,80] If (N, O)-ligands participate in the complex formation process in the $Cu_2[Fe(CN)_6]$-GIM, as in the $Ni_2[Fe(CN)_6]$-GIM, no new coordination compounds unknown for the corresponding Cu(II)-ligand systems in solution or in the solid phase are detected. The possible causes of this phenomenon have been discussed.[24] They resemble the causes discussed for the Ni(II)-(N, O)-donor atom ligand system (see Section III, 2).

2. Complex formation in the Cu(II)-(N, S)-, (O, S)-, (S, S)-ligand systems

The Cu(II)-dithiooxamide system is the most interesting and most thoroughly investigated.[25,31,58,67,72,79,133]

Analysis of the $D' = f(c_F, c_L^0, t)$ kinetic curves in terms of various coordinates[25,31] as well as the results of physicochemical studies of the substances isolated from the corresponding metal chelates matrices[79,133] permitted the conclusion that three coordination compounds are formed in the $Cu_2[Fe(CN)_6]$-GIM system, namely $[CuL(H_2O)_2]_n$,

$[Cu(HL)_2]_n$, and $[Cu(HL)_2(HL)]^-$ (H_2L^- = dithiooxamide), the first two of which are insoluble whilst the third is soluble in water. It is striking that, as for the Cu(II) – (N, O)-ligand systems, in this case complex formation in the $Cu_2[Fe(CN)_6]$ – GIM system involves the initial alkaline degradation of the MHCF in accordance with reactions (25) and (26) and only then does the incorporation of the singly deprotonated form of the ligand (HL^-) in the inner sphere of the copper(II) hydroxide coordination polymer begin.[25,31,79,133] The fact that compounds analogous to $[CuL(H_2O)]_n$ and $[Cu(HL)_2]_n$ are formed also in the complex formation reactions in the Ni(II) – dithiooxamide system is striking (see Section III, 2). According to the literature,[31,133] the monomers $CuL(H_2O)_2$ and $Cu(HL)_2$ arise initially in the Cu(II) – dithiooxamide system and then polymerise as a result of the 'cross-linking' of their molecules. In particular, for $[Cu(HL)_2]_n$ the process takes place in the following way:

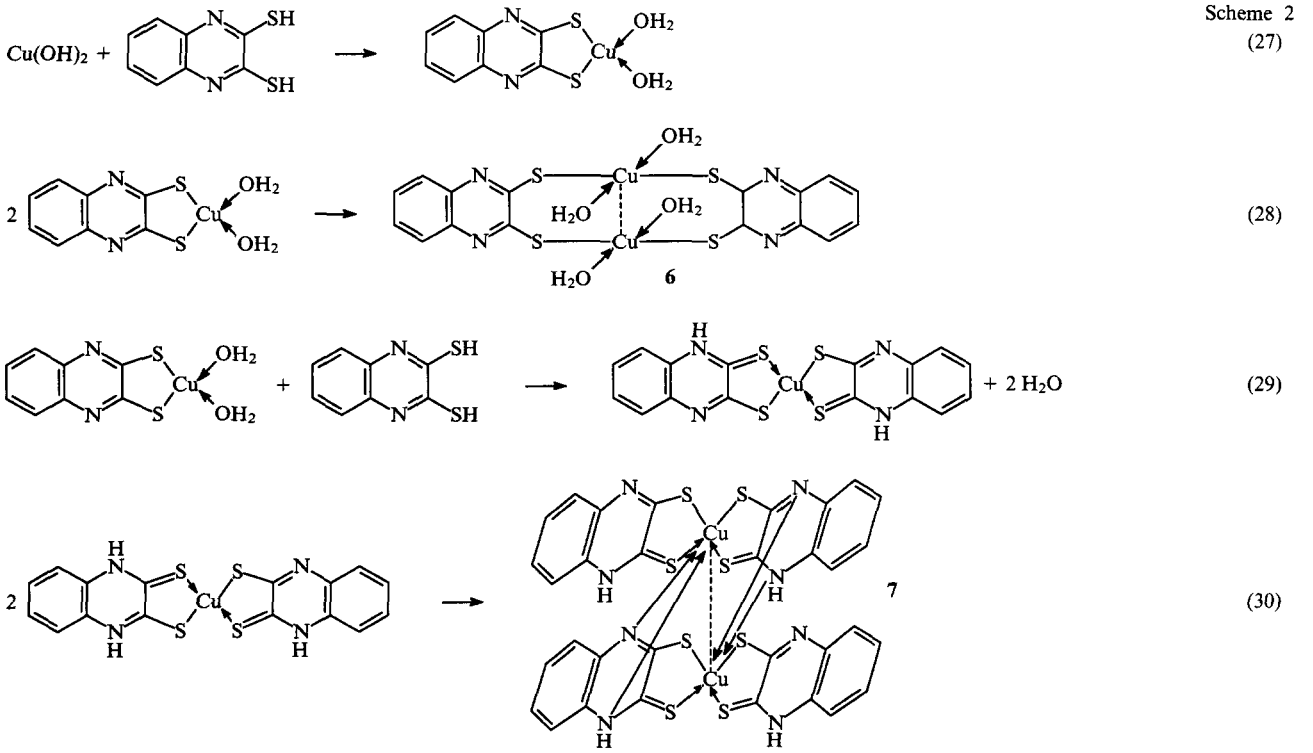


The monomeric intermediates $CuL(H_2O)_2$ and $Cu(HL)_2$ are also formed in the Cu(II) – quinoxaline-2,3-dithiol system, but ultimately the products formed in the matrix are not coordination polymers, as in the Cu(II) – dithiooxamide system, but the dimers $Cu_2L_2(H_2O)_4$ **6** and $Cu_2(HL)_4$ **7**. The diamagnetism of these compounds indicates the presence of a Cu – Cu bond in them.[31] In the case of the $Cu_2L_2(H_2O)_4$ chelate, the appearance of this bond is accompanied by the formation of two additional six-membered chelate rings ensuring a lower ground state energy than in the initial $CuL(H_2O)_2$ monomers. The formation of the dimer $Cu_2(HL)_4$ is promoted by the donor – acceptor interaction of Cu(II) with the nitrogen atoms of the quinoxaline ring, as a result of which the mutual approach of the copper chelate rings (and hence of the copper atoms), accompanied by the $\delta(3d_{xy} - 3d_{xy})$ overlap of the atomic orbitals of the Cu(II) atoms, enables the formation of the metal – metal bond.[24] The formation of the coordination compounds indicated above, based on the present author's data,[24,31] is illustrated in Scheme 2.

We may note that the ν(N – H) band in the IR spectrum of $Cu_2(HL)_4$ occurs at 3380 cm^{-1}, this frequency being characteristic of the N – H groups coordinated around the metal ion.[134] This serves as yet another piece of evidence in support of the dimeric structure of the copper(II) chelate with singly deprotonated quinoxaline-2,3-dithiol and of the presence in the latter of additional weak copper – 'quinoxaline' nitrogen coordinate bonds. It is striking that, for $c_L^0 > 10^{-1}$ M, a third ligand molecule becomes attached to the 1:2 chelates both in the Cu(II) – quinoxaline-2,3-dithiol system and in the Cu(II) – dithiooxamide system considered previously, this being accompanied by the formation of soluble compounds of the type $[Cu(HL)_2(HL)]^-$.[24,31,133] A tetragonal-pyramidal structure, in which two molecules of the ligand are bidentate, their donor atoms being located in the base of the pyramid, whilst the third molecule is monodentate and the sulfur atom coordinated to the metal ion is at the apex of the pyramid, has been postulated for these complexes.[24,133] However, neither chelate accumulates in any appreciable amounts either in the metal chelate GIM or in the solutions of the corresponding ligands in contact with them, so that the mechanism of their formation has still not been investigated in detail.

As can be seen from the foregoing, exactly as in the Cu(II) – dithiooxamide system, complex formation in the $Cu_2[Fe(CN)_6]$ – GIM in the Cu(II) – quinoxaline-2,3-dithiol system results in the formation of three coordination compounds, whereas complex formation reactions in solution or in the solid phase give rise only to chelates with the ratio H : L = 1 : 2.[98,100,102,135,136] However, in the case of the

Scheme 2

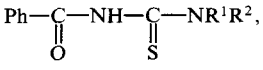


Cu(II)–*N*,*N*′-diphenylthiooxamide and Cu(II)–*N*,*N*′-diphenyldithiooxamide systems, complex formation in the $Cu_2[Fe(CN)_6]$–GIM leads to the formation of only the paramagnetic monomeric compounds $Cu(HL)_2$, as happens also under the traditional conditions.[31,79] The formation of polymeric complexes of these systems is subject to steric hindrance, as for the analogous system containing Ni(II).[31,79]

The causes of the formation in the Cu(II)–*N*,*N*′-diphenylthiooxamide and Cu(II)–*N*,*N*′-diphenyldithiooxamide systems of the monomers $Cu(HL)_2$ rather than the dimers $Cu_2(HL)_4$ [although both these ligands have, like quinoxaline-2,3-dithiol, electron-donating nitrogen atoms capable of being coordinated to Cu(II) in the complex formation reaction] are not entirely understood. It is most likely that in the monomers $Cu(HL)_2$ free rotation of the phenyl groups about the C–N bonds is possible, which hinders the mutual approach of the planar fragments of these monomeric molecules (particularly when the phenyl groups have rotated by an angle of 90° relative to the plane of the chelate ring). A similar situation arises also in the copper(II) chelate complex of dithiooxamide.[24,133] On the other hand, in the case of the monomeric $Cu(HL)_2$ complex of quinoxaline-2,3-dithiol, the phenylene groups are in the same plane as the metal chelate rings, so that steric hindrance to the mutual approach of the $Cu(HL)_2$ fragments is absent.

The formation of Cu(II) complexes with 1,2-dithiocarbamoylhydrazine and 1-carbamoyl-2-thiocarbamoylhydrazine may serve as yet another piece of evidence for the greater synthetic possibilities of complex formation in MHCF–GIM systems.[31,82] Two Cu(II) complexes have been detected in these systems—an insoluble dimeric complex and a soluble monomeric complex; on the other hand, in solution and in the solid phase only one coordination compound is produced.[100,137] These systems are of interest because with their aid it is possible to obtain nonsilver photographic images, the colour and optical-sensitometric characteristics of which are very close to the corresponding characteristics of the initial black and white silver images on silver halide light-sensitive materials.[82]

A series of new coordination compounds, previously undetected on complex formation under traditional conditions, have been discovered in the complex formation reactions of 3-benzoylthiourea derivatives having the general formula [75,76]

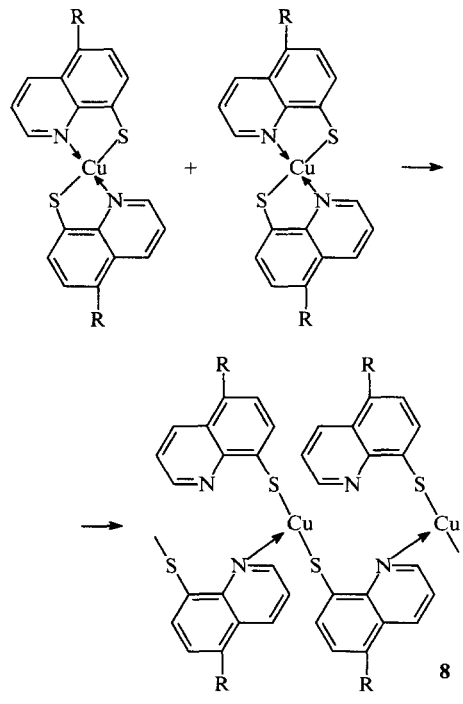


R^1, R^2 = aryl or arylalkyl.

In this connection, it is remarkable that, when the $Cu_2[Fe(CN)_6]$–GIM system is brought into contact with alkaline solutions of 1-naphthyl- and 1-(3,5-di-*tert*-butyl-4-hydroxy)phenetyl-3-benzoylthiourea, neither the formation of Cu(II) complexes with the above organic compounds nor even the alkaline degradation of copper(II) hexacyanoferrate(II) were detected in the systems.[75,76] Clearly the cumbersome nature of these ligands strongly hinders their diffusion into the polymer layer of the matrix and they therefore accumulate at the matrix–solution interface, where they create a kind of 'protecting shell', which in fact prevents the permeation of the OH^- ions into the bulk of the polymer. This phenomenon evidently requires further studies.

Under traditional conditions, the nature of complex formation in the Cu(II)–8-mercaptoquinoline and Ni(II)–8-mercaptoquinoline systems is known to be similar and only one chelate ML_2 (M = Ni, Cu; L^- = deprotonated form of 8-mercaptoquinoline) is formed in both cases.[107] A similar picture is observed also in the complex formation reaction between Ni(II) and 8-mercaptoquinoline in the corresponding metal hexacyanoferrate gelatin-immobilised matrices.[25,31] In the majority of the Cu(II)–alkyl, aryl-, or halo-8-mercaptoquinoline systems, the chelates CuL_2 are also the only products of the complex formation reaction in the MHCF–GIM.[31,35] The few exceptions include the Cu(II)–2-methyl-8-mercaptoquinoline, Cu(II)–2,7-dimethyl-8-mercaptoquinoline, and Cu(II)–2,4,6-trimethyl-8-mercaptoquinoline systems, in which the Cu(II) → Cu(I) redox process occurs, as in complex formation in solution, and hence complexes of the type CuL are formed.

In the Cu(II)–5-bromo-8-mercaptoquinoline and Cu(II)–5-methylthio-8-mercaptoquinoline systems, the formation of the monomeric chelates CuL_2 in the complex formation reaction in MHCF–GIM is accompanied by the formation at fairly high concentrations c_F and c_L^0 (>1.5 M and $>1.5 \times 10^{-2}$ M respectively) of coordination polymers having the same stoichiometric composition, which arise, according to the present author's data,[24] as a result of the 'cross-linking' of the CuL_2 monomers in accordance with the scheme



(31)

R = Br, SMe.

Such a polymer is stable only so long as it is in the reaction space of a matrix having a small volume. On the other hand, when attempts are made to isolate it from the GIM, it instantly depolymerises. However, in a gelatin-immobilised matrix at high concentrations c_F and c_L^0, the association of the CuL_2 monomers in accordance with Scheme (31) is energetically more favourable than the dissociation of the polymer formed in this way into the initial CuL_2 fragments. In contrast to the CuL_2 monomer, the coordination polymer synthesised is not a chelate and its absorption in the visible part of the spectrum is much weaker than that of the monomer. As a result of this, the $D' = f(c_F, c_L^0, t)$ (c_L^0 = const.) relations for the two systems Cu(II)–5-bromo-8-mercaptoquinoline and Cu(II)–5-methylthio-8-mercaptoquinoline systems are much more complex and have distinct maxima.[24]

It is easy to note that steric hindrance to the formation of type **8** polymeric complexes of Cu(II) with various substituted 8-mercaptoquinolines is smallest precisely when the substituent is in the 5-position, so that the formation of these polymers specifically when 5-bromo-8-mercaptoquinoline and 5-methylthio-8-mercaptoquinoline are used in the complex formation

reaction in the $Cu_2[Fe(CN)_6]$–GIM can be fully accounted for. However, the formation of such polymers in the $Cu_2[Fe(CN)_6]$–GIM has not been detected in the Cu(II)–5-chloro-8-mercaptoquinoline and Cu(II)–5,8-dimercaptoquinoline systems, as in the Cu(II)–8-mercaptoquinoline system.[24]

Presumably the absence of the polymers $(CuL_2)_n$ from the first of the above systems is associated with the lower donor capacity of the nitrogen atom in the 5-chloro-8-mercaptoquinoline molecule compared with that of 5-bromo-8-mercaptoquinoline because the chlorine atom is more electronegative and hence has a greater capacity for electron density withdrawal from the nitrogen atom. On the other hand, in 5,8-dimercaptoquinoline the sulfur atom in the 5-thiol group is a more effective electron pair donor than the sulfur atom in the methylthio-group. Because of this, at high concentrations c_F and c_L^0 in the Cu(II)–5,8-dimercaptoquinoline system, the formation of the polymer $[Cu_2L_2(H_2O)_{2n}]$, where L^{2-} is a doubly deprotonated ligand, rather than the $(CuL_2)_n$ coordination polymer indicated by Scheme (31), is more likely.[138]

It follows from the foregoing that, in complex formation reactions in the $Cu_2[Fe(CN)_6]$–GIM systems containing Cu(II) and (N, S)-, (O, S)-, and (N, S)-ligands capable of giving rise to two species differing in the degree of deprotonation, the same tendency towards the formation of coordination compounds with L^{2-} in the inner sphere is observed as in the formation of complexes in the $Ni_2[Fe(CN)_6]^-$–GIM. However, one may note at least two differences. Firstly, the complex formation reaction in the $Cu_2[Fe(CN)_6]$–GIM system proceeds in accordance with a pseudo-S_N1 mechanism and is preceded by the alkaline degradation of copper(II) hexacyanoferrate(II) in accordance with Eqns (25) and (26). For this reason, even before the start of the interaction of Cu(II) with the corresponding (N, O)- or (N, S)-ligand, the $[Fe(CN)_6]^{4-}$ anion is removed from the reaction sphere and does not enter the inner coordination sphere of the Cu(II) complexes formed. A direct consequence of this is the absence from all the Cu(II)–(N, O)-, (N, S)-, (O, S)-, or (S, S)-ligand systems investigated hitherto of 'mixed' complexes of the type $(M_2L)_2[Fe(CN)_6]$, observed in a series of Ni(II)–(N, S)-ligand systems (see Section III, 2). Secondly, the more marked tendency towards the formation of dimeric and polymeric complex species by Cu(II) compared with Ni(II) [92,96,139] is still more pronounced in the complex formation reaction in the MHCF–GIM than in solution or in the solid phase. On the other hand, overall, the data for complex formation in the $Cu_2[Fe(CN)_6]$–GIM confirm primarily the prediction that coordination dimers and polymers may be formed under these specific conditions.[35]

V. Complex formation in cobalt(II) and cobalt(III) hexacyanoferrate matrices

In contrast to nickel and copper, which form stable hexacyanoferrate(II) and stable chelate complexes with specific (N, O)-, (N, S)-, (O, S)-, or (S, S)-donor atom ligands in only one oxidation state (namely the +2 state), cobalt is capable of forming two fairly stable hexacyanoferrate complexes, $Co_2[Fe(CN)_6]$ and $KCo[Fe(CN)_6]$, and fairly stable complexes with the above ligands in which it is present in the +2 and +3 oxidation states. It is therefore useful to examine complex formation reactions in the $Co_2[Fe(CN)_6]$–GIM and $KCo[Fe(CN)_6]$–GIM systems.

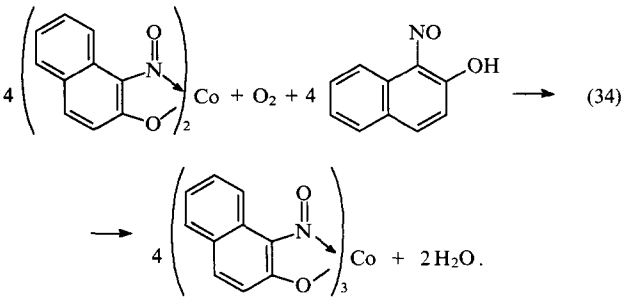
1. Complex formation in the Co(II)/Co(III)–(N, O)-ligand systems

Judging from its orbital electronegativity in aqueous solutions (+0.52 eV),[92] Co(II) is a somewhat harder Pearson acid than Ni(II) and Cu(III). Cobalt(II) belongs to the class of hard Pearson acids.[129] Both these ions have a fairly high affinity for nitrogen. They therefore form extremely readily coordination compounds with a fairly large series of (N, O)-donor atom ligands.[96,139] So far, however, more or less detailed data on complex formation in the MHCF–GIM are available only for the Co(II)–1-nitroso-2-naphthol [24,37] and Co(II)–2-nitroso-1-naphthol [24,36,37] systems. When the $Co_2[Fe(CN)_6]$–GIM comes into contact with alkaline solutions of these ligands (pH ≃ 12), the alkaline degradation of cobalt(II) hexacyanoferrate(II) takes place initially in accordance with the equations

$$\{Co_2[Fe(CN)\ ]\}_n + 2m\,OH^- \longrightarrow \longrightarrow 2[Co_n(OH)_m]^{(2n-m)+} + n[Fe(CN)\ ]^{4-}, \quad (32)$$

$$[Co_n(OH)_m]^{(2n-m)+} + (2m-n)OH^- \longrightarrow [Co(OH)_2]_n. \quad (33)$$

It is easy to see that Eqns (32) and (33) are analogous to Eqns (25) and (26) describing the degradation of $Cu_2[Fe(CN)_6]$ by OH^- ions. Subsequently, the polymeric cobalt(II) hydroxide interacts both with 1-nitroso-2-naphthol and with its isomer 2-nitroso-1-naphthol; the only product is then CoL_2.[24,36,37] It was shown in the studies quoted above that, for $c_F < 0.15$ M, $c_L^0 > 1.0 \times 10^{-2}$ M, and $t \geqslant 10$ min, CoL_2 is partially oxidised by atmospheric oxygen to the corresponding cobalt(III) chelate. In particular, in the case of 1-nitroso-2-naphthol this process proceeds in accordance with the equation [24]



In terms of the nature of the $D' = f(c_F, c_L^0, t)$ relations, the Co(II)–8-hydroxyquinoline and Co(II)–α-benzoin oxime systems are close to the Co(II)–1-nitroso-2-naphthol and 2-nitroso-1-naphthol systems. Similar complex formation reactions probably take place in them.[37] When the $Co_2[Fe(CN)_6]$–GIM system comes into contact with an alkaline solution of dimethylglyoxime, the gelatin layer initially acquires a violet colour, which vanishes after 20 s. According to Mikhailov and Polovnyak,[37] this unusual phenomenon is associated with the oxidation of the dimethylglyoxime chelate $Co(HL)_2$ (violet in colour) formed initially to the corresponding colourless and water-soluble chelate $Co(HL)_3$, which is removed from the matrix when the latter comes into contact with the ligand solution.

In contrast to the Co(II)–(N, O)-ligand systems already considered, complex formation in the $Co_2[Fe(CN)_6]$–GIM has not been detected in any of the Co(III)–(N, O)-ligand systems [where the (N, O)-ligands were 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 8-hydroxyquinoline, and α-benzoin oxime]. It has been suggested that the reason for this phenomenon arises from the extremely high thermodynamic stability of cobalt(III) hexacyanoferrate(II) and the fact that ligand exchange between the inner sphere of the cobalt(III) hexacyanoferrate(II) coordination polymer and the (N, O)-ligands is difficult.

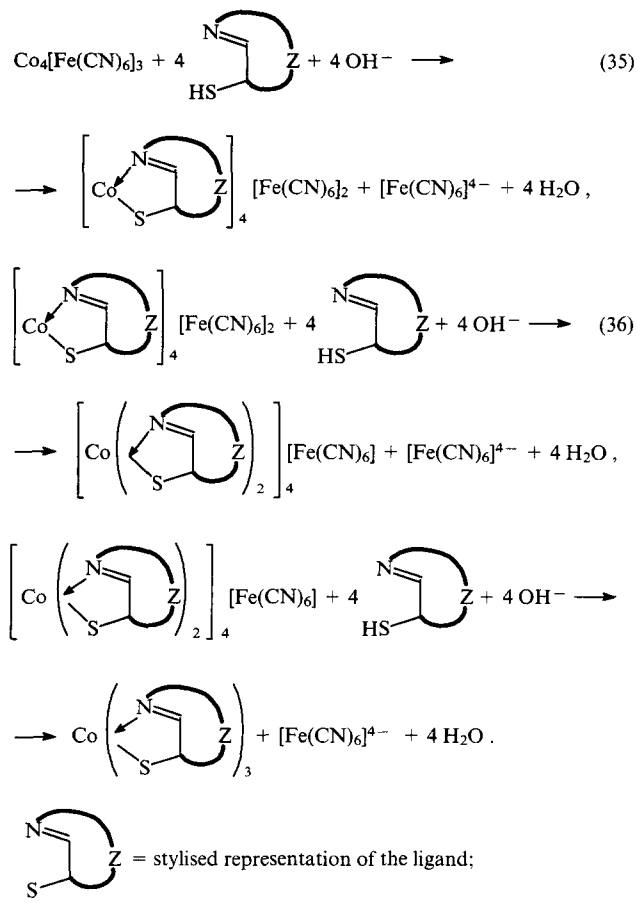
2. Complex formation in the Co(II)/Co(III)–(N, S)-, (O, S)-, (S, S)-ligand systems

According to the present author's data,[24] the nature of the $D' = f(c_F, c_L^0, t)$ relations in the Co(II)–dithiooxamide, Co(II)–*N,N'*-diphenyldithiooxamide, Co(II)–*N,N'*-diphenyldithiooxamide, Co(II)-quinoxaline-2,3-dithiol, and Co(II)-8-mercaptoquinoline systems for complex formation in the $Co_2[Fe(CN)_6]$–GIM is the same as that discussed above in the Co(II)–(N, O)-donor atom ligand systems. Accordingly, the

alkaline degradation of $Co_2[Fe(CN)_6]$ in accordance with Schemes (32) and (33), the formation of the chelates $Co(HL)_2$ (HL^- is the singly deprotonated ligand), and their subsequent oxidation by atmospheric oxygen to the corresponding chelates $Co(HL)_3$ are observed in all these systems when the $Co_2[Fe(CN)_6]$-matrix comes into contact with solutions of the (N, S)-ligands listed above. However, in contrast to complex formation in the MHCF–GIM in the Co(II)–(N, O)-ligand systems, in the case of the (N, S)-ligands the cobalt(II) complexes are in fact intermediates and do not accumulate in any appreciable amounts in the matrices whatever the values of c_F, c_L^0, and t.[24,35] In this connection, one should note that, according to the results of a whole series of investigations,[116,118,119,127,140,141] the complex formation reactions between cobalt(II) and dithiooxamide, its *N,N'*-substituted derivatives, and quinoxaline-2,3-dithiol in solution result in the formation of the chelates $Co(HL)_2$ or CoL_2, which are fairly resistant to oxidation. The fact that the chelates CoL_2 formed in the $Co_2[Fe(CN)_6]$–GIM are detected only as intermediates has been attributed[24] to the high dispersity of cobalt(II) hexacyanoferrate(II) in the matrix and the high concentration of OH^- ions in the system, which increases the probability of the oxidation of Co(II) to Co(III) in the MHCF–GIM compared with solution. As in the $Cu_2[Fe(CN)_6]$–GIM, the complex formation reaction in the $Co_2[Fe(CN_6]$–GIM takes place in accordance with a pseudo-S_N1 mechanisms.[25,35] For the same reasons as in the case of the $Cu_2[Fe(CN)_6]$–GIM, no sphere complexes of any kind with OH^- or $[Fe(CN)_6]^{4-}$ anions arise in the $Co_2[Fe(CN)_6]^-$–GIM on complex formation in the Co(II)–(N, S)-, (O, S)-, and (S, S)-ligand systems.[24,25,35]

As regards complex formation in the Co(III)–(N, S)-, (O, S)-, and (S, S)-ligand systems in the cobalt(III) hexacyanoferrate(II)–GIM, the situation is on the whole much more complex.[25,35] The clearer evidence for this is provided by the complex formation reaction in the Co(III)–dithiooxamide system, which has been investigated in detail.[25,38,65] It was noted that the complex formation in this system proceeds in accordance with an S_N2 mechanism and is accompanied by multistage elimination of the $[Fe(CN)_6]^{4-}$ anion from the inner sphere of the cobalt(III) hexacyanoferrate(II) coordination polymer. This results in gradual complex formation, giving rise to the sparingly soluble chelates $[Co(HL)]_4[Fe(CN)_6]_2$, $[Co(HL)_2]_4[Fe(CN)_6]$, and $Co(HL)_3$ (HL^- is the singly deprotonated ligand). The ratios of these complexes in the matrix depend both on the values of c_F, c_L^0, and t and on the degree of dispersity of elemental silver in the silver-containing matrices from which the cobalt(II) hexacyanoferrate(II) matrices have been obtained.[25,38,65] It is therefore extremely difficult to predict the final result of the complex formation reaction for a particular set of parameters c_F, c_L^0, and t.

The situation is complicated further also by the fact that, at fairly high ligand concentrations in solution and for prolonged contact between the matrix and the solution in the Co(III)–dithiooxamide system, the soluble complex $[Co(HL)_2(HL)_2]^-$ also appears. An octahedral structure of this compound with two monodentate and two bidentate ligand molecules has been postulated.[38] The bidentate molecules are coordinated to Co(III) via the nitrogen and sulfur atoms, while the monodentate ligands are coordinated via the sulfur atoms. Similar sparingly soluble chelates with the metal : ligand = 1 : 1, 1 : 2, and 1 : 3 ratios have been detected also in the Co(III)–*N,N'*-diphenylthiooxamide, Co(III)–*N,N'*-diphenyldithiooxamide,[25,38] and Co(III)-8-mercaptoquinoline[24,25] systems. According to data of Mikhailov and Budnikov,[25] their formation reactions can be described by the following general equations:



It is noteworthy that that 1 : 1 and 1 : 2 chelates have not been detected in the complex formation reactions in solution and in the solid phase.[106,140] Apart from these types of complexes, the formation of the complex $(Co_2L)_2[Fe(CN)_6]$ in the Co(III)–*N,N'*-diphenylthiooxamide system has also been postulated.[38] The following remarkable factor is striking in this connection. As already stated above, Ni(II) and Cu(II) form fairly stable coordination chelate compounds with the L^{2-} forms of dithiooxamide and *N,N'*-diphenylthiooxamide. However, Co(III) has a higher charge and a smaller radius than Ni(II) and Cu(II), so that the Co(III) chelates formed with the HL^- forms of both these ligands should be more effective proton donors, like the chelates with the corresponding form of *N,N'*-diphenyldithiooxamide, than the analogous Ni(II) and Cu(II) chelates. It can therefore be expected that the probability of the formation of the Co(III) chelates with the L^{2-} forms of all the above three ligands is much greater than the probability of the formation of the corresponding Ni(II) and Cu(II) chelates.

However, the HL^- forms and not the L^{2-} forms of the above ligands are in fact present in the inner spheres of virtually all the Co(III) compounds with dithiooxamide *N,N'*-diphenylthiooxamide, and *N,N'*-diphenyldithiooxamide synthesised by the complex formation reactions in the cobalt(II) hexacyanoferrate(II)–GIM. This paradox may be accounted for by the fact that theoretically the *trans*-HL^- or *trans*-L^{2-} forms of the above ligands with nitrogen and sulfur donor atoms should participate in the formation of the complexes of Co(III), since the latter is a harder Pearson acid than Ni(II) and Cu(II), and not the *cis*-HL^- or *cis*-L^{2-} forms (with two donor sulfur atoms), as happens in the case of Ni(II) and Cu(II).[24] On the other hand, the participation of the *trans*-L^{2-} forms in the complex formation reaction automatically presupposes that any of the above ligands is tetradentate and hence this should lead theoretically to the formation of polymeric chelates. However, the formation of

polymeric structures by Co(III), involved exclusively in octahedral coordination, with the tetradentate *trans*-L^{2-} forms of such ligands is sterically hindered, whereas the formation of chelates with the bidentate *trans*-HL^{-} forms does not encounter such hindrance. In all the Co(III) chelate complexes with dithiooxamide, *N*,*N'*-diphenylthiooxamide, and *N*,*N'*-diphenyldithiooxamide formed by complex formation reactions in the cobalt(III) hexacyanoferrate(II) matrix, the ligands are coordinated to the metal ion via the nitrogen and sulfur atoms.[24,35] One can therefore expect that complex formation in the MHCF–GIM should not occur in the Co(II)-quinoxaline-2,3-dithiol system, where the ligand is a structurally rigid analogue of dithiooxamide and contains only sulfur atoms as the donor centres.[24,35,38]

In conclusion one should note that the nature of complex formation in the cobalt(III) hexacyanoferrate(II)–GIM in all the Co(III)–(N, S)-ligand systems investigated is independent of the number of species with different degrees of deprotonation formed by the ligand.[24,25,35,38] This constitutes a sharp difference between complex formation reactions in the cobalt(III) hexacyanoferrate(II)–GIM, on the one hand, and in the nickel(II) and copper(II) hexacyanoferrate(II) matrices, on the other, where such a dependence can be seen (see Sections III, 2 and IV, 2) to be quite distinct. One can also conclude that, overall, the characteristic features of complex formation in the cobalt(III) hexacyanoferrate(II)–GIM clearly confirm the validity of the prediction that intermediate coordination compounds, which are not detected under the 'traditional' conditions (see Section II, 2), can be formed under the specific conditions of the MHCF–GIM.

VI. Complex formation in the iron(III) hexacyanoferrate(II) matrix

The uniqueness of the situation consists in the fact that the metal-containing components of this MHCF–GIM contain ions of the same 3*d* element in different oxidation states [Fe(II) and Fe(III)]. Each of them is potentially capable of forming complexes mainly with 'hard' donor centres.

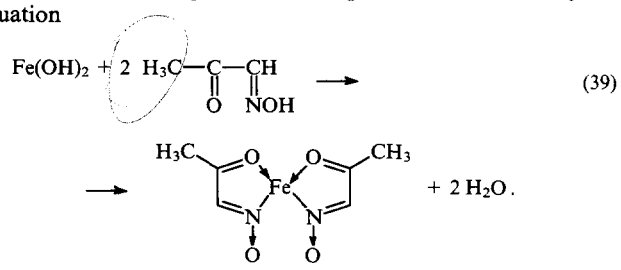
1. Complex formation in Fe(II, III)–(N, O)-ligand systems

The Fe(II) and Fe(III) atoms present in $KFe[Fe(CN)_6]$ belong to the category of moderately hard and hard Pearson acids respectively[129] (their orbital electronegativities in aqueous solution are +0.69 and +2.22 eV respectively).[92] Their extremely stable complexes with (N, O)-ligands such as 8-hydroxyquinoline, nitrosonaphthols and their derivatives,[105] oximes,[104] and complexones,[100,101] are known. However, only two of these — 8-hydroxyquinoline[70,72] and isonitrosoacetone $H_3CC(O)CH{=}NOH$ — have so far been used in complex formation reactions in the $KFe[Fe(CN)_6]$–GIM. The study of complex formation in the $KFe[Fe(CN)_6]$–GIM system is extremely seriously restricted by the fact that the Fe(II) and Fe(III) complexes formed with ligands containing both nitrogen and oxygen usually absorb extremely weakly in the visible part of the spectrum, have relatively low stability constants, and dissolve appreciably in water.[29,72] It has been shown in the studies quoted that, when the $KFe[Fe(CN)_6]$–GIM comes into contact with alkaline solutions of the above ligands ($pH \geqslant 12$), the alkaline degradation of the metal-containing component of the MHCF–GIM takes place initially in accordance with the equations

$$KFe[Fe(CN)_6] + 3\,OH^- \longrightarrow FeO(OH) + [Fe(CN)_6]^{4-} + K^+ + H_2O\,, \quad (37)$$

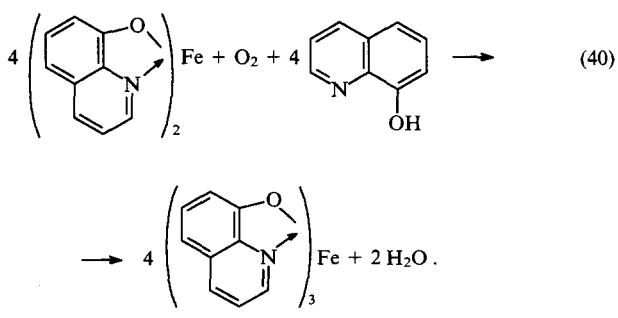
$$KFe[Fe(CN)_6] + 2\,OH^- \longrightarrow Fe(OH)_2 + [Fe(CN)_6]^{3-} + K^+\,. \quad (38)$$

This results in the formation of a mixture of Fe(II) and Fe(III) oxide hydroxides in the GIM, the ratio of which probably depends very significantly both on the experimental conditions and on the degree of dispersity of iron(III) hexacyanoferrate(II) in the immobilised matrix.[24] However, only the Fe(II) hydroxo-complexes interact with each of the ligands indicated above.[29,70] The $D' = f(c_F, c_L^0, t)$ curves for the Fe(II)–isonitrosoacetone system are extremely simple: with increase in $c_F t$ and c_L^0 (at a fixed concentration c_F), the optical densities of the polymer layer of the matrix increase monotonically, tending to certain limiting values which depend on c_F.[70] According to Mikhailov and Polovnyak,[70] the complex formation process is described by the equation



(39)

The chelate FeL_2 is virtually the only complex formation product also in the Fe(II)–8-hydroxyquinoline system.[70] However, in this case the $D' = f(c_F, c_L^0, t)$ relations are somewhat more complex than in the Fe(II)–isonitrosoacetone system: in particular, for $c_F < 0.3$ M and $c_L^0 > 1.0 \times 10^{-2}$ M, with increase in t the quantities D' begin to decrease after attaining a certain maximum value.[70,72] This finding has been attributed[29,70,98,142] to the occurrence in the system under consideration of the Fe(II) → Fe(III) redox process in accordance with the overall scheme

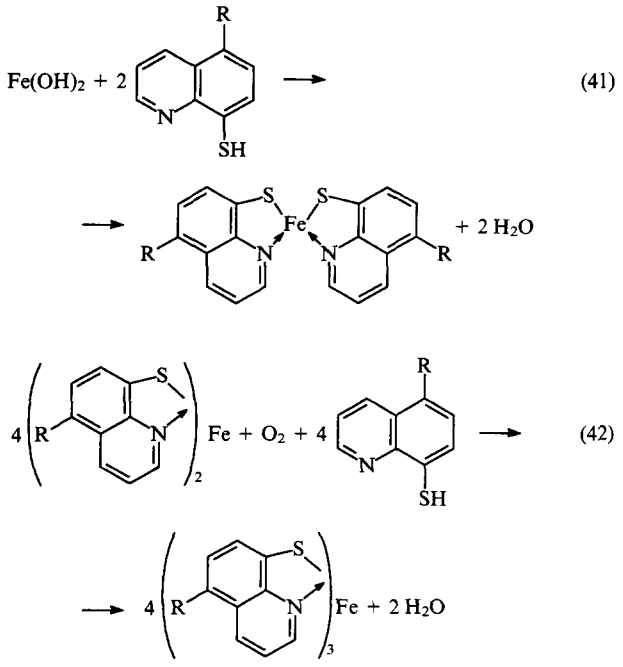


(40)

It has been stated that the natures of the $D' = f(c_F, c_L^0, t)$ curves for the Fe(II)–1-nitroso-2-naphthol and Fe(II)–2-nitroso-1-naphthol systems are similar to those for the Fe(II)–isonitrosoacetone system, but these systems have not been characterised in greater detail.[24,70]

2. Complex formation in the Fe(II), (III)–(S, S)-, (N, S)-, and (O, S)-ligand systems

There are also hitherto extremely few examples of complex formation in the Fe(II)–(N, S)-ligand systems under the specific conditions which obtain in the $KFe[Fe(CN)_6]$-GIM. There are data on complex formation in the iron(III) hexacyanoferrate(II) matrix when the latter comes into contact with aqueous alkaline solutions of 8-mercaptoquinoline and its 5-bromo- and 5-methylthio-derivatives.[24] In all three cases, three ligand molecules become attached in succession to one $Fe(OH)_2$ fragment during the complex formation process, the third molecule being attached much more slowly than the first two. It has been suggested that initially Fe(II) complexes with the corresponding ligands arise in all the iron(II)–ligand systems indicated, but the complexes are instantaneously oxidised by atmospheric oxygen to the corresponding Fe(III) coordination compounds.



(41)

(42)

It is striking that the chelates FeL_3 are formed in all these cases actually from $Fe(OH)_2$ and not from FeOOH or some other iron(III) oxide hydroxide.[24] On the other hand, one should note that, when the $KFe[Fe(CN)_6]$-GIM comes into contact with alkaline solutions of ligands such as dithiooxamide, *N*,*N*′-diphenylthiooxamide or *N*,*N*′-diphenyldithiooxamide, quinoxaline-2,3-dithiol, 1,2-dithiocarbamoylhydrazine, and 1-carboxyl-2-thiocarbamoylhydrazine, only the alkaline degradation of iron(III) and potassium hexacyanoferrates(II) is detected and no Fe(II) and Fe(III) coordination compounds with the ligands indicated are produced.[25,29] In contrast to complex formation in the $M_2[Fe(CN)_6]$-GIM [M = Ni(II), Cu(II), Co(II)] and the $KCo[Fe(CN)_6]$-GIM, in the complex formation reaction in the $KFe[Fe(CN)_6]$ matrices it was not possible to detect in any of the systems considered any kind of new coordination compounds which had not been detected previously in the interaction of Fe(II) with the corresponding ligands in solutions or in the solid phase.[35,70,98] The high lability of the high-spin Fe(II) and Fe(III) chelates and also the low probability of the formation of dimeric and polymeric species with the ligands considered by both iron(II) and iron(III) have been specified as the probable causes of this phenomenon.[24,29]

To a first approximation, all the 3*d* element-chelating (N,O)-, (N,S)-, (O,S)-, and (S,S)-ligand systems described in the literature can be quite definitely assigned to one of two types of complex formation: in the first of these, the process proceeds by a formal S_N2 mechanism [systems in which the metal-containing components are nickel(II) and cobalt(III) hexacyanoferrates(II)], while in the second it proceeds via a formal pseudo-S_N1 mechanism [systems in which the metal-containing components are copper(II), iron(III), and cobalt(II) hexacyanoferrates(II)]. Both homoligand and heteroligand {i.e. containing ligand molecules deprotonated to a particular extent and the $[Fe(CN)_6]^{4-}$ anion} chelate complexes may be formed in systems of the first type. Only homoligand coordination compounds are formed in systems of the second type and, despite the fact that theoretically there is a possibility in this instance of the existence of complexes containing in the inner coordination sphere any of the forms of the ligands indicated above as well as the OH^- group, their appearance has not been detected in the complex formation reaction in the MHCF-GIM in any of the systems examined in the literature.

Only one variant of complex formation is as a rule characteristic of each of the metal hexacyanoferrate(II)-GIM considered. Depending on the nature of the ion of the 3*d* element (but regardless of the nature of the ligand), the formation of the above heteroligand complexes in such a variant either always occurs [in the complex formation reaction occurring in the cobalt(III) hexacyanoferrate(II)-GIM] or, on the contrary, it never occurs [in the complex formation reaction in the cobalt(II) hexacyanoferrate(II)-GIM]. Only the $Ni_2[Fe(CN)_6]$-GIM is an exception, where complex formation can take place in accordance with one or another variant depending on the nature of the ligand. The first variant occurs for ligands containing nitrogen, which are capable of generating under the complex formation conditions at least two species with different degrees of deprotonation, while the second occurs in the case of ligands containing both nitrogen and sulfur, which give rise to only one deprotonated species, and also in the case of ligands containing both nitrogen and oxygen. One can therefore conclude that the nature of the differences between the complex formation reactions in solutions and in the metal hexacyanoferrate(II) gelatin-immobilised matrix systems is fully consistent with the predictions which can be made on the basis of the considerations described in Section II, 2.

VII. Practical possibilities for complex formation reactions in metal hexacyanoferrate(II) matrices

1. The production of nonsilver photographic images on silver halide photosensitive materials

The process involving the formation of nonsilver photographic images consists of three stages: (1) bleaching of the silver image obtained on the photographic material by means of its standard treatment[26-28] in a solution containing potassium hexacyanoferrate(III), the soluble salt of a 3*d* element ion (as a rule the chloride or sulfate), and any organic hydroxyacid (citric, oxalic [sic], or tartaric); (2) fixation of the bleached image by treating the photographic emulsion with an aqueous solution of sodium thiosulfate; (3) toning of the image by treating the photographic emulsion with an alkaline solution of the corresponding chelating organic compound. In terms of the composition of the solutions used to treat the photographic materials and the chemistry of the processes occurring, the first two stages correspond to the synthesis of the MHCF-GIM and the third to the complex formation reaction in such GIM.[35] It is noteworthy that in a number of instances the nonsilver photographic image obtained from the metal chelates can be produced also by a shorter procedure: the exposed silver halide photographic material is initially developed and then subjected to treatment involving the successive operations 1-3. It is then possible to shorten the time required to obtain the nonsilver metal chelate image and also to improve the efficiency and accelerate the oxidation of the elemental silver to the corresponding silver(I) compounds [the hexacyanoferrate(II) or the chloride).[143] Several tens of technological processes of this type have already been described in the literature. The main bulk of the publications have been devoted to the synthesis of nonsilver images from nickel(II) chelates;[40,41,43,49,53,57,58,60,66,68,69,71,72,74,77,78,81] and a somewhat smaller number have been devoted to the synthesis of images from copper(II) chelates;[36,39,42,46,50,51,54,55,58,62,67,72,75,76,79,80] on the other hand, instances of the employment of the chelates of other 3*d* elements are the carriers of nonsilver images are encountered much more rarely.[36-38,44,47,48,56,63,65,72] In particular, technologies for the production of nonsilver images by means of carriers such as the nickel(II) chelate complexes of dimethylglyoxime,[40,77] dithiooxamide and its *N*,*N*′-diphenyl derivatives,[41,57,58,64,66,69,71] and *N*,*N*′-diphenylthiooxamide,[53,78] the copper(II) chelate complexes of α-benzoin oxime,[46,60] 8-hydroxyquinoline,[50] and dithiooxamide,[39,64,72,79] the cobalt(II) chelate complexes of nitrosonaphthols,[36,37,44] the cobalt(III) chelate complex of dithiooxamide,[38,45,65] and the iron(II) complex of 8-hydroxyquinoline.[45,70]

The formation of nonsilver images from nickel(II) chelate complexes of dithiooxamide is the most interesting process.[40,58,64,66,69,71,72] It has been used, in particular, for the preparation of 'blue slides'.[58] This procedure for the preparation of 'blue slides' is less laborious and, what is most important, is less demanding as regards external conditions compared with the familiar traditional processes based on organic dyes.[143] The dark blue or blue images obtained from the $[Ni(HL)_2]_n$ chelate complexes of dithiooxamide are distinguished by a greater purity of the light lines, greater contrast, and greater photostability. Yet another important quality of this procedure is that, in contrast to all the other processes for the intensification of photographic images known hitherto,[26] in many cases it does not increase but actually diminishes the degree of fogging compared with the initial silver image.[40,58,64] The cause of this phenomenon is closely associated with the occurrence of process (23).

The above phenomenon is fairly typical for technologies for the synthesis of nonsilver images from the chelates of 3*d* elements. It is observed, in particular, also in the formation of images from the copper(II) chelate complex of dithiooxamide (dark-green),[39,64,79] the copper(II) chelate complex of 1,2-dithiocarbamoylhydrazine (black),[50,82] the copper(II) chelate complex of 1-carbamoyl-2-thiocarbamoylhydrazine (black-brown),[51,82] and the cobalt(III) chelate complex of dithiooxamide (amber-yellow).[38,48,65] It is striking that the images generated by the copper(II) chelate complex of 1,2-dithiocarbamoylhydrazine[50,82] and the iron(III) complex of 8-hydroxyquinoline[45,70] 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 colour of the image.

One should note especially that the employment of all these technologies makes it possible to vary widely the photographic characteristics of the treated materials. In particular, by altering the concentrations and the 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.[72] Review articles have been published on the problem under consideration.[72,143]

2. Synthesis of test objects for the measurement of optical absorption spectra

A fundamentally new variant of the preparation of test objects has been developed with the aid of complex formation in the MHCF–GIM systems. Its significant features reduce to the fact that the substance analysed is synthesised in a gelatin layer as a result of a series of specific chemical reactions.[144–146] In particular, test objects comprising nickel(II)–dimethylglyoxime, copper(II)–dithiooxamide, cobalt(II)-2-nitroso-2-naphthol, and iron(II)–8-hydroxyquinoline coordination compounds have been prepared in this way. In principle, the ideas underlying this method can be used to prepare also test objects comprising a series of other inorganic compounds, in particular oxides and sulfides.[144] This method is probably fairly promising also for the preparation of test objects comprising certain organic compounds which absorb intensely in the visible part of the spectrum.[145]

3. Modelling of complex formation in bulk-phase polymers

There are indications in the literature that complex formation in a MHCF–GIM system may serve as a useful model for the interpretation of the stabilising effect of certain antioxidants for polymeric materials, in particular derivatives of 3-benzoylthiourea. Such a stabilising effect reduces to the 'complexing' of the microimpurities comprising the ions of the 3*d* elements, for example copper(II), present in bulk-phase polymers.[138,147] However, the study of this problem is in the initial stage.

VIII. Conclusion

It follows from the foregoing that complex formation in the metal hexacyanoferrate(II) gelatin-immobilised matrix systems is a specific phenomenon in chemical science in general and in coordination chemistry in particular. A new field of science has arisen—involving the study of the reactivities of polymer-immobilised coordination compounds with fixation of the substance by means of intermolecular forces and the study of the characteristics of complex formation involving such compounds. In essence, only the first steps have been taken on these lines, but it is already evident that complex formation under the nontraditional conditions described can lead to the formation of coordination compounds the existence of which investigators have sometimes not even suspected. There is no doubt that, as the range of the metal–ligand systems employed within the framework of the 'classical' complex formation expands, the very considerable potential synthetic possibilities of complex formation in metal hexacyanoferrate(II)-GIM as well as its possible practical applications will be manifested to a much greater extent.

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