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Complexing Processes on the Immobilized Matrices of Hexacyanoferrate(II) Copper(II) and Nitrogen-Sulfur-Containing Ligands in Thin Gelatin Layer

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Summary. Complexing processes occurring between immobilized matrices obtained from Cu(II) hexacyanoferrates(II) and solutions of various nitrogen-sulfur-containing chelating ligands in thin gelatin layers have been studied. With $Cu_2[Fe(CN)_6]$-matrix, the complexing process is found to proceed according to pseudo-S_N1-mechanism. The schemes of the processes in each of the above matrices are given. Examples of kinetic curves for particular systems "hexacyanoferrate(II)copper(II)-ligand" are presented.

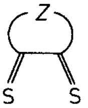
Keywords. Immobilized matrix; Complexing; Thin gelatin layer.

Komplexierungsprozesse auf den immobilen Matrices von Hexacyanoferrat(II)-Kupfer(II) und N-S-haltigen Liganden in dünnen Gelatin-Schichten

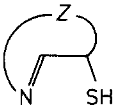
Zusammenfassung. Es wurden Komplexierungsprozesse auf immobilisierten Matrices, die von Cu(II)-Hexacyanoferrat(II) und Lösungen verschiedener Stickstoff-Schwefel-Liganden erhalten wurden, in dünnen Gelatin-Schichten untersucht. Mit einer $Cu_2[Fe(CN)_6]$-Matrix wurde festgestellt, daß der Komplexierungsprozeß nach einem Pseudo-S_N1-Mechanismus verläuft. Es werden die entsprechenden Reaktionsschemata angegeben. Beispiele für den kinetischen Verlauf für bestimmte „Hexacyanoferrat(II)-Cu(II)-Ligand"-Systeme werden präsentiert.

Introduction

One of the most important problems of modern silver halide photography is the substitution of silver constituting photographic images for other, less costly but available organic or inorganic compounds. One of the possible ways of the transformation of the silver image into a non-silver one, is the process where the image carriers are intensively coloured inorganic compounds, and first of all, coordination compounds of various metals. The possibility of utilization of Ni(II) coordination compounds with nitrogen-sulfur-containing ligands formed as result of heterogeneous complexing on hexacyanoferrate(II) nickel(II) matrices immobilized in thin gelatin layers, in the course of reactions with aqueous solutions of nitrogen-sulfur-containing ligands, as carriers of photographic images have previously been pointed out [1]. In the present paper, complexing processes observed on Cu(II) hexacyanoferrate(II) matrices during the reaction with the solution of bidentate ligands types **I**–**III** are investigated, where Z is either a closed-ring system or an open-ring group of atoms.



I



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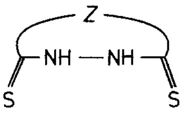


III

Experimental Part

Matrices containing hexacyanoferrate(II) copper(II) ($Cu_2[Fe(CN)_6]$) were obtained on the basis of conventionally formed silver images (by the development and fixation of the silver halide photographic material) [2] by means of a two-stage chemical treatment. The first stage includes oxidation of elemental silver into its hexacyanoferrate(II), together with the co-precipitation of $Cu_2[Fe(CN)_6]$ upon reaction with the copper(II) ion with citric or oxalic acid [3, 4]:

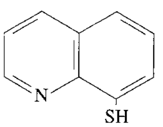
$$6[Cu(Ct)_2]^{2-} + 4\,Ag + 4[Fe(CN)_6]^{3-} + 12\,H^+ \rightarrow 3\,Cu_2[Fe(CN)_6] + Ag_4[Fe(CN)_6] + 12\,HCt^{3-}\,, \tag{1}$$

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

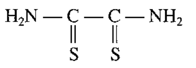
(H_4Ct is citric acid, H_2Ox is oxalic acid). The second stage involves the transition of $Ag_4[Fe(CN)_6]$ into the solution upon the reaction with an aqueous thiosulfate solution according to (3) with the formation of a water-soluble complex:

$$Ag_4[Fe(CN)_6] + 8\,S_2O_3^{2-} \rightarrow 4[Ag(S_2O_3)_2]^{3-} + [Fe(CN)_6]^{4-}\,. \tag{3}$$

Between the stages, as well as upon the completion of the second stage, the material comprising a metal hexacyanoferrate(II) matrix was washed with running water for a few minutes, and then the matrix was processed in alkaline solutions of sulfur-containing ligands such as 8-mercaptoquinoline (1) and its halide, alkyl S-methyl derivates, dithiooxamide (2), its N,N′-diphenyl substituted derivative, quinoxaline-2,3-dithiol (3), bis(thiocarbamyl)hydrazine (4) and its N,N′-dialkylsubstituted derivative.

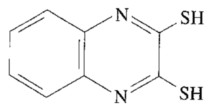


1



$H_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH_2$

2



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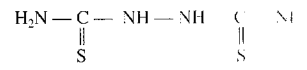


$H_2N-\underset{\underset{S}{\|}}{C}-NH-NH\ \underset{\underset{S}{\|}}{C}\ \ NH_2$

4

The ligand concentrations in the solutions varied in the range of $10^{-3}-10^{-1}\,mol/dm^{-3}$, the pH value was maintained at 12.0 ± 0.1, since these parameters provide a high concentration of the thiol form of ligands, which is directly involved in complexing processes. The matrices were kept in solution for about 1–10 min at 20°C. Optical densities of thin gelatin layers containing chelate complexes copper(II) with these ligands were measured on a "MACBETH TD-504" densitometer (Kodak Co., U.S.A.) in the region of 0.1–4.0 with an accuracy of ±2% (relatively). The absorption spectra were measured on a "Specord" spectrophotometer in the region 10 000–30 000 cm^{-1} (350–1 000 nm). Using the results of the measurements, kinetic curves were plotted with D as a function of C_F, C_L and t, $D=f(C_F, C_L, t)$, where D is the density of a thin gelatin layer containing the chelate complex formed upon the chemical processing of the immobilized matrix, C_L is the ligand concentration in solution, C_F is the concentration $Cu_2[Fe(CN)_6]$ in the immobilized matrix, t is the complexing process time. Examples of such relationships are given in Figs. 1–4. An analysis of the relationships allows to draw conclusions which are given in the section below.

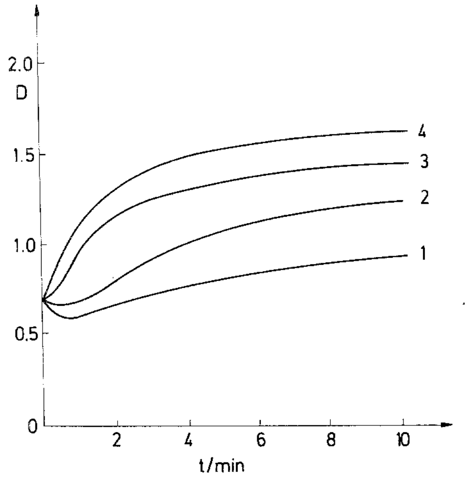


Fig. 1. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Cu_2[Fe(CN)_6]$-matrix-8-mercaptoquinoline; fixed Cu(II) hexacyanoferrate(II) concentration ($C_F = 1.5 \cdot 10^{-2}\,mol\,m^{-2}$) in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $6.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*1*), $1.2 \cdot 10^{-2}\,mol\,dm^{-2}$ (*2*), $3.0 \cdot 10^{-2}\,mol\,dm^{-2}$ (*3*) and $5.0 \cdot 10^{-2}\,mol\,dm^{-3}$ (*4*); optical densities measured through a green filter with a transmission maximum at 540 nm

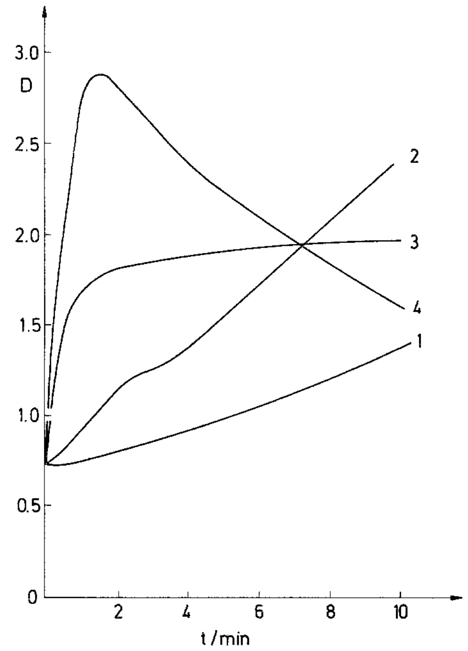


Fig. 2. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Cu_2[Fe(CN)_6]$matrix-dithiooxamide; fixed Cu(II) hexacyanoferrate(II) concentration ($C_F = 1.5 \cdot 10^{-2}\,mol\,m^{-2}$) in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $1.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*1*), $4.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*2*), $7.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*3*), and $2.0 \cdot 10^{-2}\,mol\,dm^{-3}$ (*4*); optical densities measured through a green filter with a transmission maximum at 540 nm

Results and Discussion

In the systems containing Cu(II) hexacyanoferrate(II) matrix, a complexing process according to a pseudo-S_N1 mechanism with the ligand entering in the inner coordination sphere is preceded by the decomposition of hexacyanoferrate(II) molecules into corresponding hydroxide, according to (4):

$$Cu_2[Fe(CN)_6] + 4\,OH^- \rightarrow Cu(OH)_2 + [Fe(CN)_6]^{4-}\,. \qquad (4)$$

The reaction (4) is not observed at the contact of $Ni_2[Fe(CN)_6]$-immobilized matrices with alkaline solutions of all the studied ligands [1]. Actually the ligand interact with copper(II) hydroxide. Two different types of ligand-hexacyanoferrate(II) matrices interaction can be distinguished. In a number of cases, when a ligand is capable of forming only the singly deprotonated form, in the complexing process insoluble chelates with a metal/ligand ratio of 1 : 2 are formed. This phenomenon is observed in the case of such ligands as 8-mercaptoquinoline (**1**) and its derivatives and N,N′-diphenylsubstituted dithiooxamide and N,N′-diphenyl-

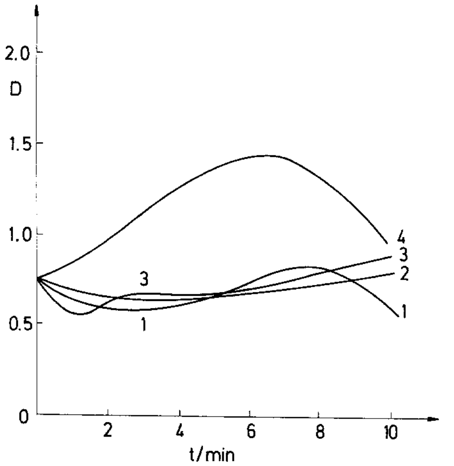


Fig. 3. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Cu_2[Fe(CN)_6]$-matrix-quinoxaline-2,3-dithiol; fixed Cu(II) hexacyanoferrate(II) concentration ($C_F = 1.5 \cdot 10^{-2}\,mol\,m^{-2}$) in the gelatin layer, variable complexing process time t, and ligand concentrations C_L in the solution $2.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*1*), $4.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*2*), $6.0 \cdot 10^{-3}\,mol\,dm^{-3}$ (*3*), and $2.0 \cdot 10^{-2}\,mol\,dm^{-3}$ (*4*); optical densities measured through a green filter with a transmission maximum at 540 nm

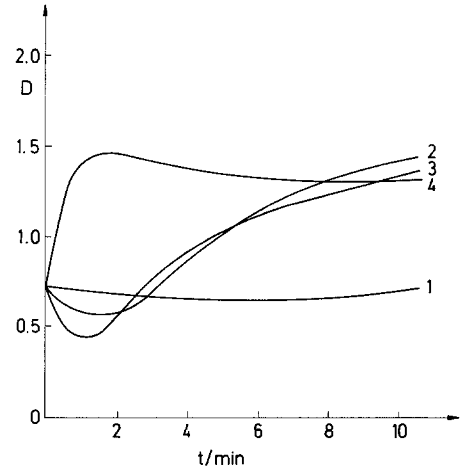
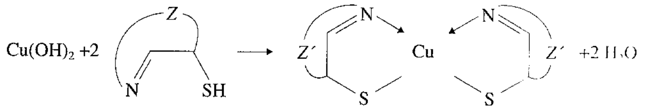


Fig. 4. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Cu_2[Fe(CN)_6]$-matrix-bis(thiocarbamyl)hydrazine; fixed Cu(II) hexacyanoferrate(II) concentration ($C_F = 1.5 \cdot 10^{-2}\,mol\,m^{-2}$) in the gelatin layer, variable complexing process time t, and ligand concentrations C_L in the solution $1.2 \cdot 10^{-3}\,mol\,dm^{-3}$ (*1*), $3.2 \cdot 10^{-3}\,mol\,dm^{-3}$ (*2*), $6.5 \cdot 10^{-3}\,mol\,dm^{-3}$ (*3*), and $2.5 \cdot 10^{-2}\,mol\,dm^{-3}$ (*4*); optical densities measured through a green filter with a transmission maximum at 540 nm

substituted bis(thiocarbamyl)hydrazine. The splitting of the second proton of these molecules is theoretically possible but practically very difficult.

Such chelates do not decompose considerably even under the influence of excessive ligand concentrations in solution directly containing the thin gelatin layer. For the 8-mercaptoquinoline and its 5-substituted derivatives, the formation process can be described by the general equation (5):

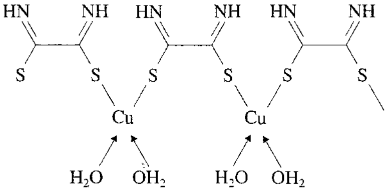


(5)

where Z' is the singly deprotonated group Z.

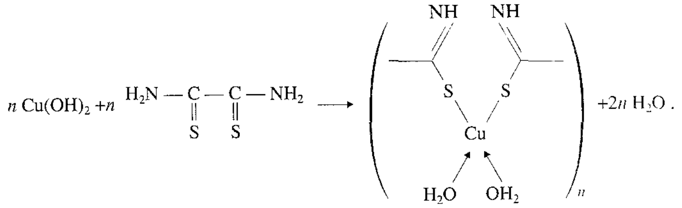
The chelates thus formed are usually yellow-brown or (which is rare) green-yellow; absorption spectra in thin gelatin layers containing the above complexes demonstrate the "wings" of intensive bands of charge transfer from the ligand to a metal at $\nu_{max} = 28\,000 - 30\,000\,cm^{-1}$ ($\lambda_{max} = 330 - 350\,nm$), as well as the bands in the blue region of the visible spectrum at $21\,000 - 23\,000\,cm^{-1}$ ($\lambda_{max} = 430 - 470\,nm$) and the red region of the visible spectrum at $\nu_{max} = 15\,000 - 16\,000\,cm^{-1}$ ($\lambda_{max} = 620 - 670\,nm$). In the case when a ligand is capable of forming a doubly-deprotonated form, another variant of complexing is observed. In the $Cu_2[Fe(CN)_6]$-dithiooxamide system two types of insoluble chelates having a partially or completely (singly or doubly) deprotonated form of the ligand are obtained.

If the ligand is scarce, an insoluble 1 : 1 chelate having a doubly-deprotonated ligand form which is of the brown-green colour with a very sloping maximum at $\nu_{max} = 14\,500 - 15\,000\ cm^{-1}$ ($\lambda_{max} = 670 - 690\ nm$) is formed. This complex has practically the same absorption in the whole visible spectrum region. This complex does not change its colour and optical characteristics by influence of alkaline or acide solutions. It should be noted that in the $Ni_2[Fe(CN)_6]$-dithiooxamide system, at high hexacyanoferrate(II) nickel(II) and high ligand concentrations, an insoluble 1 : 1 chelate with completely deprotonated ligand form is formed. This complex is uncapable of proton addition; this is connected with the characteristics of a coordination polymer [1]. Therefore, it may be presumed that the brown-green chelate copper(II) with dithiooxamide is also a coordination polymer (**IV**).



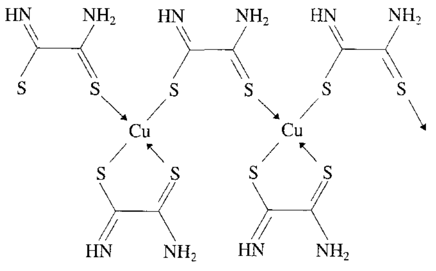
IV

The formation process can be described by the following scheme:



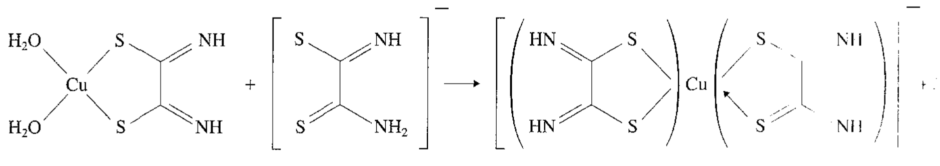
(6)

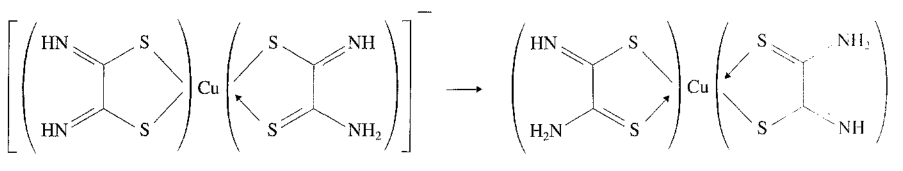
It is noteworthy that in the $Cu_2[Fe(CN)_6]$-dithiooxamide system the formation of chelate Cu(II) with completely-deprotonated ligand form cannot be observed, in contrary to that for the $Ni_2[Fe(CN)_6]$-dithiooxamide system. This fact, however, is quite explicable if one takes into account the dimeric and polymeric complex formation [in comparison with Ni(II)] [5]. At high ligand concentrations of a solution in contact with a $Cu_2[Fe(CN)_6]$-matrix one obtains a complex with copper(II) ion/ligand ratio of 1 : 2 which has a doubly deprotonated ligand form in the inner coordination sphere. This complex, however, adds immediately two protons and is transformed into the insoluble copper(II) chelate with its singly deprotonated form 1 : 2. This compound is of dark-green colour and has a very broad "plateau" in the visible spectrum region at $\nu = 14\,000 - 20\,000\ cm^{-1}$ ($\lambda_{max} = 500 - 700\ nm$). The above mentioned copper(II) chelate is also stable in acidic and alkaline solutions. This is in accordance with the structure of a coordination polymer **V**:



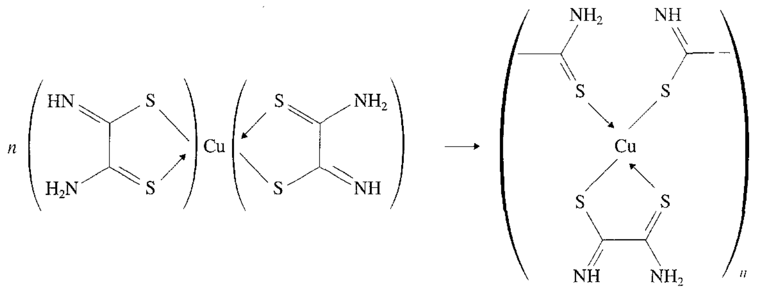
V

The formation process of this compound can be described by Eqs. (7) − (9),



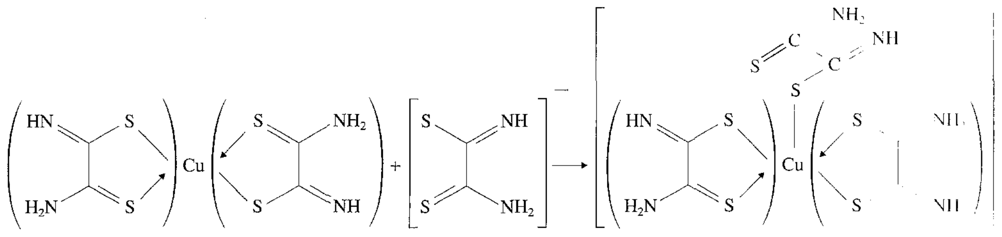


(8)



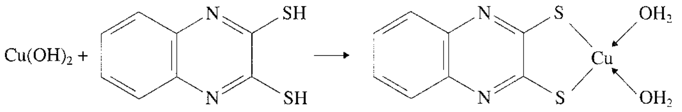
(9)

In the $Cu_2[Fe(CN)_6]$-dithiooxamide system, the copper(II) chelate with two molecules of singly- and doubly-deprotonated ligand form is not accumulated to a great extent. In view of the fact that this complex is soluble in water, a little part of molecules of the above mentioned complex diffuse from the thin gelatin layer into the ligand solution in contact with the $Cu_2[Fe(CN)_6]$-matrices without deprotonation. Moreover, in this case the entering of the third ligand molecule into the inner coordination sphere of monomeric chelates 1 : 2 (with two molecules of the singly deprotonated form of dithiooxamide) takes place. As a result, a soluble complex with the characteristics for a Cu(II) tetragonal pyramide structure **VI** is formed,

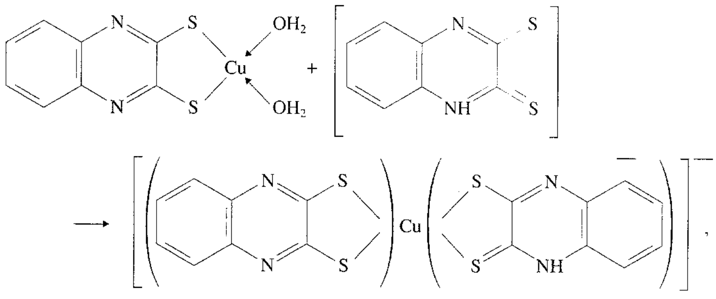


VI (10)

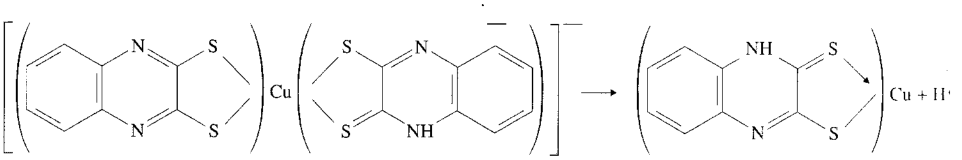
Due to this fact, for high ligand concentrations the optical densities D (as functions of time) of the thin gelatin layer have a maximum. The kinetic curves $D = f(t)$ in the $Cu_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol are also characterized by an extremum. Moreover, in these curves one can observe an essential decrease of the optical densities D at relatively small values of C_L and t which can be explained by reaction (4). In this system, a copper(II) chelate 1 : 1 is formed if the ligand is scarce and the chelate 1 : 2 is formed at sufficiently high C_L. Both complexes contain the doubly-deprotonated ligand. However, the chelate complex 1 : 2 with doubly-deprotonated form of bis(thiocarbamyl)hydrazine has a lower proton-accepting ability than the analogous compound in the $Cu_2[Fe(CN)_6]$-dithiooxamide system. This complex 1 : 2, with the doubly-deprotonated ligand form is transformed comparatively slow into chelate 1 : 2 with the singly-deprotonated ligand form. The chelate complex 1 : 2 with doubly-deprotonated form is enough well soluble in water, and it diffused out noticably of thin gelatin layer into the solution contacting the $Cu_2[Fe(CN)_6]$-matrices. These two circumstances are a cause of the peculiar dependence of $D = f(t)$ for the $Cu_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol system. It is interesting to note that in the $Cu_2[Fe(CN)_6]$-dithiooxamide system the copper(II) chelates are 1 : 1 (with doubly-deprotonated ligands form) and 1 : 2 (with singly deprotonated ligands form), forming coordination polymers; in $Cu_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol these chelates are coordination monomers, since steric effects prevent the polymerization. Their formation process can be described by schemes (11)–(13),



(11)

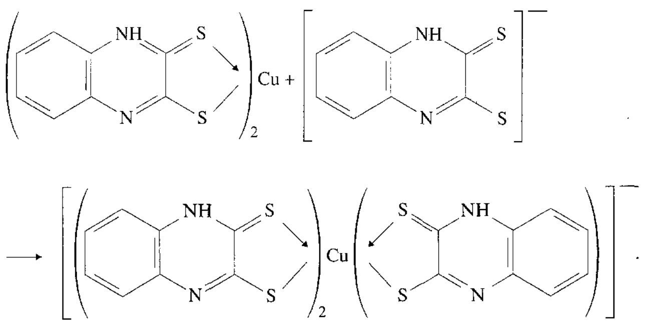


(12)



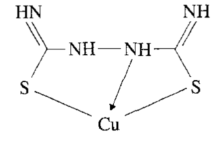
(13)

The chelates thus formed usually possess a brown (1 : 1) or yellow-brown (1 : 2) colour. Absorption spectra of the above complexes demonstrate the "wings" of intensive bands of charge transfer from the ligand to a metal at $\nu_{max} = 28\,000 - 30\,000\,cm^{-1}$ ($\lambda_{max} = 330 - 350\,nm$). As in the $Cu_2[Fe(CN)_6]$-dithiooxamide system the coordination of additional ligands to the chelate 1 : 2 according to scheme (14) is also observed. In this connection, it should be noted that in the $Ni_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol system the soluble complex forms are not observed [1],

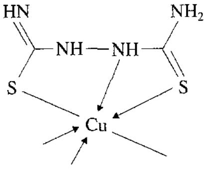


(14)

A similar situation is also obtained in the $Cu_2[Fe(CN)_6]$-bis(thiocarbamyl)-hydrazine system. However, some distinctions are observed. The most appreciable distinction is that here in the region $t > 6\,\text{min}$ D values either are practically constant or a little increased (in the $Cu_2[Fe(CN)_6]$-dithiooxamide and $Cu_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol systems in this region of $t > 6\,\text{min}$ D values for high ligand concentrations with time increase are decreased). This phenomenon is explained by the absence of the reaction analogous to the reactions (10) and (14). The insoluble chelates with a copper(II) ion/ligand ratio of 1 : 1 (with completely ligand form) and with copper(II) ion/ligand ratio of 1 : 2 (with partially ligand form) have brown-black colour. These both compounds are coordination monomers as chelates 1 : 1 and 1 : 2 in the $Cu_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol system. However, in the $Cu_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol the formation of coordination polymers prevent steric factors, in the $Cu_2[Fe(CN)_6]$-bis(thiocarbamyl)hydrazine the formation of coordination polymers prevent thermodynamic factors (since the polymerization of monomeric chelates 1 : 1 and 1 : 2 should be accompanied with destruction of chelate cycles **VII** and **VIII** which are thermodynamically not favoured):



VII



VIII

The complexing processes described in this paper can be used for mono- and polychromatic toning of silver images in the silver-halogen-photographic materials in various variations of yellow, brown or green colour. Moreover, owing to these complexing processes a considerable increase of the photographic sensitivity and optical densities of images is gained, with these characteristics for silver-halogen-materials with silver images. This positive effect most appreciably is observed for the images which contained copper(II) chelate with dithiooxamide [4]. Due to this, the formation process of chelates of Cu(II) with dithiooxamide in thin gelatin layer has been realized for the increase of optical densities of images in the photographic materials for X-ray and radiography [6].

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