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3d-Element Coordination Compounds with Bidentate Sulfur-Containing Ligands as Possible Carriers of Non-Silver Photographic Images

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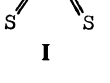
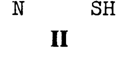
Complexing processes occurring between reactive matrices obtained from Fe(III), Co(III), Ni(II), Cu(II) hexacyanoferrates(II), and alkaline solutions of various nitrogen-sulfur-containing chelating ligands in thin gelatin layers have been studied. With Fe(III) and Cu(II) hexacyanoferrates, complexing process is found out to proceed according to S_N1 mechanism, while in Co(III) and Ni(II) hexacyanoferrates matrices, S_N2 mechanism is realized. The schemes of the processes proceeding in each of the above matrices are given. The examples of the kinetic curves for particular systems "hexacyanoferrate(II)-ligand" as well as spectral characteristics of thin gelatin layers containing chelate complexes formed as a result of the chelating process are presented. The possibility of practical utilization of complexing processes studied for obtaining non-silver photographic images from light-resistant metallorganic dyes is reported.

Modern chemical photographic industry is known to be one of the largest silver-consuming industries which spends annually about 30% of the total output of this precious metal.1) One of the ways of overall cutting down the silver consumption in this branch of technology is the so called silver recovery. One of the methods of silver recovery process consists in the following: being a "working material" for the formation of a photographic image, by means of a number of specific chemical reactions, silver is substituted for chelate complexes of 3d-elements having various nitrogen-sulfur-containing ligands intensively absorbing in the visible spectrum region. Due to this process, it becomes possible to form in the initial silver halide photographic material non-silver images characterized by an extremely high light resistance and stability towards detrimental atmospheric attacks (oxygen, sulfuric compounds etc.). From the chemical point of view, the formation of non-silver images with such carriers is nothing but a heterogenous complexing process, and the investigation of the latter presents both academic and practical interest.

In the present paper methods of electron spectroscopy and spectrophotometry were used to investigate the processes of heterogenous complexing occurring in thin layers of various silver halide materials containing previously formed and uniformly dispersed in the gelatin binding agent reactive matrices obtained from Fe(III), Co(III), Ni(II), and Cu(II) hexacyanoferrates(II) upon the reaction with alkaline solutions of chelating ligands of types **I** and **II**:



I



II

(where Z is a closed-ring or open-ring group of various atoms).

Experimental

Matrices containing metal hexacyanoferrates(II) were obtained on the basis of the conventionally formed silver images (by the development and fixation of the silver halide photographic material),2) by means of the two-stage chemical treatment. The first stage includes oxidation of elemental silver into its hexacyanoferrate(II) or halide, alongside with the co-precipitation of Fe(III), Co(III), Ni(II), and Cu(II) hexacyanoferrates(II) upon the reaction with solutions containing potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$, and a complex with a corresponding metal ion with a certain oxyacid, according to the following schemes (1—4):3—6)

$$2Fe_2(HCt)(HTart) + 4[Fe(CN)_6]^{3-} + 4Ag + 3K^+ \rightarrow 3KFe[Fe(CN)_6]+Ag_4[Fe(CN)_6]+[Fe(HTart)_2]^{3-}+2HCt^{3-} \quad (1)$$

$$4[Co(HCt)_2]^{3-} + 4[Fe(CN)_6]^{3-} + 4Ag + 4Cl^- \rightarrow Co_4[Fe(CN)_6]_3 + 4AgCl + 8HCt^{3-}+[Fe(CN)_6]^{4-} \quad (2)$$

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

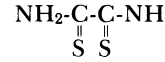
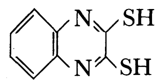
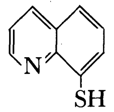
$$6[Cu(ox)_2]^{2-} + 4[Fe(CN)_6]^{3-} + 4Ag \rightarrow 3Cu_2[Fe(CN)_6]+Ag_4[Fe(CN)_6]+12ox^{2-} \quad (4)$$

(here H_2ox, H_4Ct, and H_4Tart are oxalic, citric, and tartaric acids, respectively).

The second stage involves the transition of $Ag_4[Fe(CN)_6]$ and AgCl into the solution upon the reaction with an aqueous thiosulfate solution according to schemes (5 and 6) at the expense of the formation of a water-soluble complex:

$$Ag_4[Fe(CN)_6]+8S_2O_3^{2-} \rightarrow 4[Ag(S_2O_3)_2]^{3-}+[Fe(CN)_6]^{4-} \quad (5)$$

$$AgCl+2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} +Cl^- \quad (6)$$

Between the stages, as well as upon the completion of the second stage, the material comprising a metal hexacyanoferrate(II) matrix was washed by the running water for a few minutes, and then the matrix was processed in alkaline solutions of sulfur-containing ligands such as dithiooxamide  $NH_2\text{-}\underset{S}{\overset{}{C}}\text{-}\underset{S}{C}\text{-}NH_2$, its *N,N′*-diphenyl-substituted derivative, 2,3-quinoxalinedithiol  (which can be regarded as a thiol form of a substitution product of two hydrogen atoms for 1,2-phenylene in a dithiooxamide molecule), 8-quinolinethiol  and its 5-chloro- and 5-methylthio derivatives. Ligand concentration in the solution varied in the range of 10^{-3}—10^{-1} mol·dm^{-3}, pH value was maintained at 12.0±0.1, since these parameters provide for the large accumulation of the thiol form of ligands directly involved in heterogenous complexing processes. Besides, a relatively high physicomechanical strength of the gelatin layer is preserved in which a non-silver image is formed. Matrices were kept in alkaline solutions for about 1—10 min at 20 °C. Optical densities of thin layers containing chelate complexes were measured on a "Macbeth TD-504" densitometer (Kodak Co., USA) in the region (0—4) with an accuracy of ±2% (rel.); the absorption spectra were measured on a SPECORD spectrophotometer in the region 10000—30000 cm^{-1} (350—1000 nm). Using the result of the measurements, kinetic curves were plotted in $D=f(D^{Ag})$ coordinates (where D^{Ag} is the density of a thin gelatin layer containing elemental silver. D is the density of a thin layer containing chelate complex formed upon the chemical processing of the gelatin layer having D^{Ag} density) for various time-concentration conditions of heterogenous complexing processes using Fe(III), Co(III), Ni(II), and Cu(II) hexacyanoferrate(II) matrices containing the above mentioned ligands. The examples of such relationships are given in Figs. 1—4. The analysis of these $D=f(D^{Ag})$ relationships enables one to make certain conclusions which are given in the section below.

Results

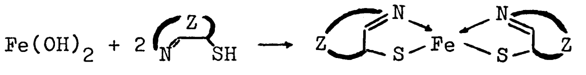
In case of the systems containing Fe(III) and Cu(II) hexacyanoferrate(II) matrices, heterogenous complexing occurs according to pseudo-S_N1 mechanism where ligand entering the internal coordination sphere is preceded by the decomposition of hexacyanoferrate(II) molecules into the corresponding hydroxides, according to schemes (7,8) and (9), respectively.

$$2KFe[Fe(CN)_6]+6OH^- \rightarrow Fe_2O_3+2[Fe(CN)_6]^{4-}+2K^++3H_2O \qquad (7)$$

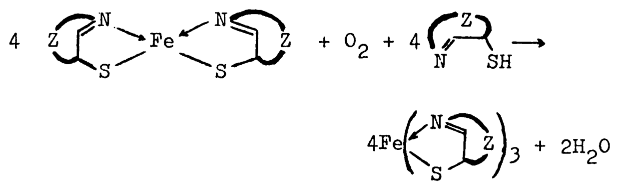
$$KFe[Fe(CN)_6]+2OH^- \rightarrow Fe(OH)_2+[Fe(CN)_6]^{3-}+K^+ \qquad (8)$$

$$Cu_2[Fe(CN)_6]+4OH^- \rightarrow 2Cu(OH)_2+[Fe(CN)_6]^{4-} \qquad (9)$$

On a Fe(III) hexacyanoferrate(II) matrix, heterogenous complexing was observed only with type II ligands, with the formation of compounds having metal ion/ligand ratio equal to 1 : 3. The process of their formation, unlike other matrices, occurs in the presence of molecular oxygen and consists of two stages, provided that initially formed Fe(II) chelates are oxidized into Fe(III) chelates, which impart to thin



(10)



(11)

gelatin layers different shades of the redbrown color and give absorption in the region of 450—480 nm. For Cu(II) hexacyanoferrate(II) matrices under similar conditions, insoluble 1 : 2 chelates are formed which in a number of cases (e.g. with dithiooxamide or 2,3-quinoxalinedithiol) with an excessive ligand concentration are capable of passing into soluble forms and subsequently diffuse from the thin gelatin layer to a contacting alkaline solution of the respective ligand. The chelates thus formed usually acquire a yellow-brown color or (which is rare) a green-yellow color; absorption spectra of thin gelatin layers containing the above compounds demonstrate the "wings" of intensive bands of charge transfer from the ligand to a metal in the region of 330—370 nm, as well as the bands in the blue (460—490 nm) and the red (620—670 nm) visible spectrum regions. The exception is a dark-green Cu(II) chelate containing dithiooxamide which does not show distinct λ_{max} values. The process of Cu(II) chelate formation can be described by

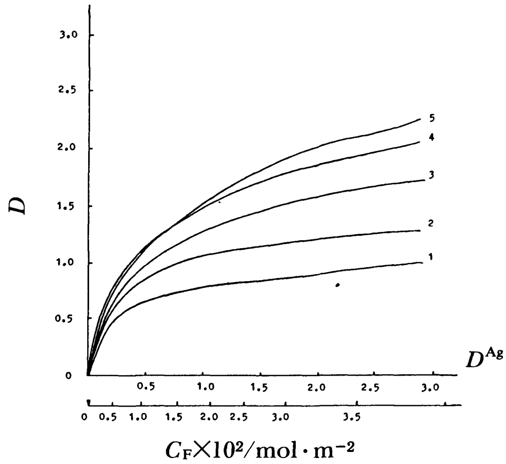


Fig. 1. Kinetic curves in $D=f(D^{Ag})$ coordinates for the system containing KFe[Fe(CN)$_6$]-8-quinolinethiol matrix at the fixed (3×10^{-2} mol·dm^{-3}) ligand concentration in the solution and variable Fe(III) hexacyanoferrate(II) concentrations in the gelatin layer for the complexing process of different durations: 1 min—curve 1; 2 min—2; 4 min—3; 6 min—4; 10 min—5 at 20 °C. Optical densities were measured through the yellow filter with a transmission in the visible spectrum region from its long-wave boundary to 590 nm. C_F is the concentration of hexacyanoferrate(II) in mol·m^2·10^{-2}.

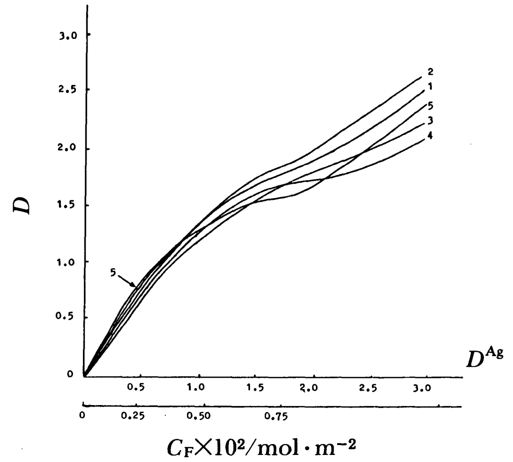


Fig. 2. Kinetic curves in $D=f(D^{Ag})$ coordinates for the system containing $Co_4[Fe(CN)_6]_3$-*N,N'*-diphenyldithiooxamide matrix at the fixed (4×10⁻³ mol·dm⁻³) ligand concentration in the solution and variable Co(III) hexacyanoferrate(II) concentrations in the gelatin layer for the complexing process of different durations: 1 min—curve 1; 2 min—2; 4 min—3; 6 min—4 and 10 min—5 at 20 °C. Optical densities were measured through the red filter with a transmission maximum at 670 nm.

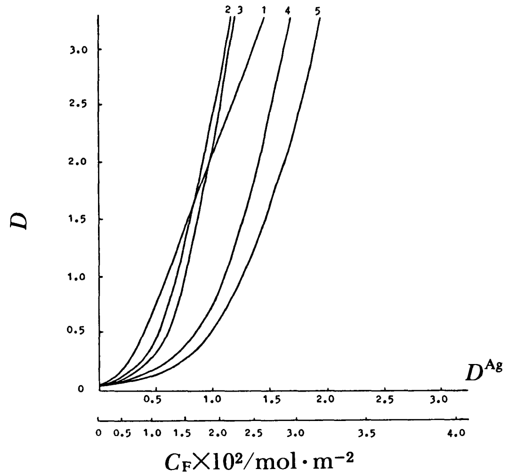
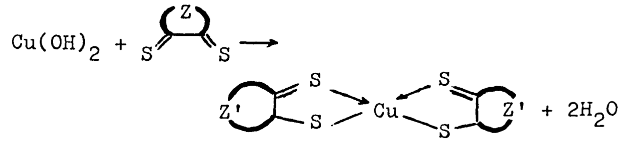


Fig. 3. Kinetic curves in $D=f(D^{Ag})$ coordinates for the system containing $Ni_2[Fe(CN)_6]$-dithiooxamide matrix at the fixed (2×10⁻² mol·dm⁻³) ligand concentration in the solution and variable Ni(II) hexacyanoferrate(II) concentrations in the gelatin layer, for the complexing process of different durations: 1 min—curve 1; 2 min—2; 4 min—3; 6 min—4; 10 min—5 at 20 °C. Optical densities were measured through the green filter with transmission maximum at 540 nm.

the equation similar to (10) which for type I ligands acquires the form of (12);



(12)

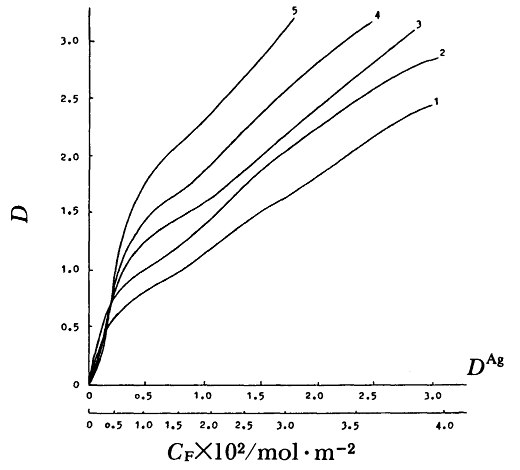
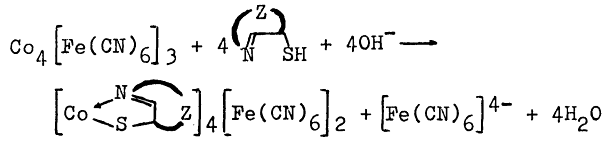


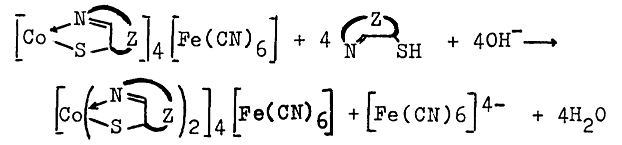
Fig. 4. Kinetic curves in $D=f(D^{Ag})$ coordinate, for the system containing $Cu_2[Fe(CN)_6]$-2,3-quinoxalinedithiol at the fixed (6×10⁻³ mol·dm⁻³) ligand concentration in the solution and variable Cu(II) hexacyanoferrate(II) concentrations in the gelatin layer, for the complexing process of different durations: 1 min—curve 1; 2 min—2; 4 min—3; 6 min—4; 10 min—5 at 20 °C. Optical densities were measured through the blue filter with transmission maximum at 450 mm.

(Z′ is a deprotonated group Z).

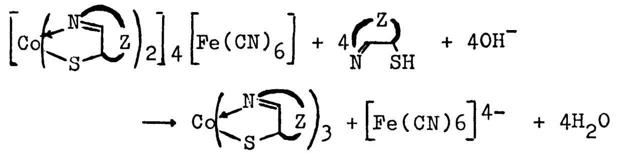
In case of $Co_4[Fe(CN)_6]_3$ and $Ni_2[Fe(CN)_6]$ matrices where S_N1 mechanism of ligand addition is realized, quite another way of heterogenous complexing is observed. In Co(III) hexacyanoferrate(II) matrix, a stepwise addition of ligands takes place, together with the formation of compounds having Co(III) ion/ligand ratio of 1 : 1, 1 : 2, and 1 : 3. The above process is accompanied by a somewhat peculiar change in optical densities of the thin gelatin layer which at first tend to increase, then decrease and finally again are observed to increase; this phenomenon is obviously connected with the relation of molar absorption coefficients (ε_{max}), such as $\varepsilon_{1:1}>\varepsilon_{1:2}<\varepsilon_{1:3}$. The chelates thus formed are of yellow, red-brown or brown colors, and they usually have either maximum at 400—460 nm or contain in the visible spectrum only the "wings" of charge transfer intensive bands coming from UV-region. In this case, complexing process can be described by the equations (13—15) (given for the ligands of type **II**):



(13)

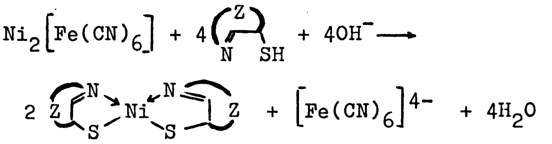


(14)



(15)

Of special importance is Ni(II) hexacyanoferrate(II) for which two different types of a ligand-hexacyanoferrate(II) matrix interaction can be distinguished. In the processes of the first type, such as heterogenous complexing in $Ni_2[Fe(CN)_6]$-8-quinolinethiol or its substitutes, insoluble chelates having a metal/ligand ratio of 1 : 2 with a singly deprotonated form of a ligand are formed. Such chelates do not decompose significantly even under the influence of excessive ligand concentrations in a solution directly contacting the thin gelatin layer. The color of such chelates is usually from pink to violet in the region 500—550 nm. It should be noted that with pH change, these chelates do not change their optical characteristics; for the ligands of type **II**, the formation process can be described by the general Eq. 16



(16)

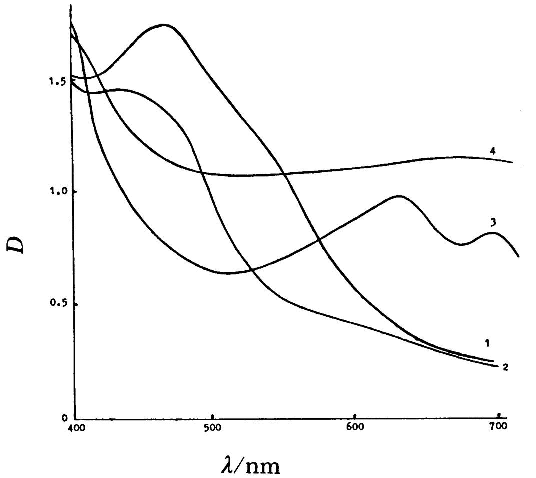


Fig. 5. Spectral characteristics of thin gelatin layers containing: 1—Fe(III) chelate with 8-quinolinethiol ($C_F=0.3\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 3.0×10^{-2} mol·dm^{-3}, duration of complexing reaction is 2 min at 20 °C); 2—Co(III) chelate with dithiooxamide ($C_F=0.4\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 1.0×10^{-2} mol·dm^{-3}, duration of complexing reaction is 4 min at 20 °C); 3—Ni(II) chelate with 2,3-quinoxalinedithiol ($C_F=3.5\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 2.0×10^{-2} mol·dm^{-3}, duration of complexing reaction is 6 min at 20 °C); 4—Cu(II) chelate with dithiooxamide ($C_F=4.0\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 4.0×10^{-3} mol·dm^{-3}, duration of complexing reaction is 4 min at 20 °C). The thickness of layers is 20000 nm (20 μm).

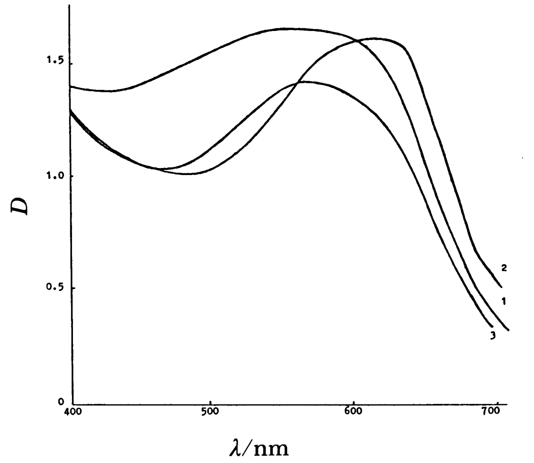
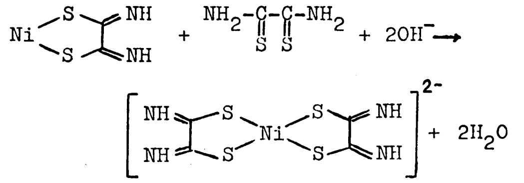


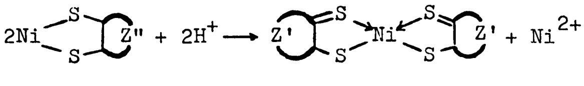
Fig. 6. Spectral characteristics of thin gelatin layers containing: 1—Ni(II) chelate with dithiooxamide of 1 : 1 ratio comprizing a completely ionized ligand form in the internal sphere ($C_F=1.5\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 8.0×10^{-3} mol·dm^{-3}, duration of complexing reaction is 6 min at 20 °C); 2—Ni(II) chelate with dithiooxamide of 1 : 2 ratio (Structure **III**) ($C_F=4.0\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 4.0×10^{-3} mol·dm^{-3}, duration of complexing reaction is 2 min at 20 °C); 3—Ni(II) chelate with dithiooxamide of 1 : 1 ratio (Structure **V**) ($C_F=4.0\times10^{-2}$ mol·m^{-2}, ligand concentration in the solution is 3.5×10^{-2} mol·dm^{-3}, duration of complexing reaction is 10 min at 20 °C). The thickness of layers is 20000 nm (20 μm).

In a number of cases when a ligand is capable of forming a double-deprotonated form, another variant of heterogenous complexing is possible which can be found in systems containing $Ni_2[Fe(CN)_6]$-dithiooxamide and $Ni_2[Fe(CN)_6]$-2,3-quinoxalinedithiol, where two types of insoluble chelates having a partially or completely deprotonated form of the ligand are obtained. For systems of the first type, at a highly excessive ligand concentration, the initially formed insoluble 1 : 1 complex can pass into the soluble one diffusing from the gelatin layer into the solution; the process is accompanied by the decrease in optical densities of the thin layer:



(17)

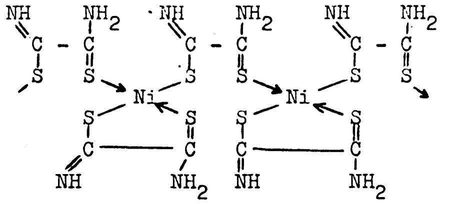
It is interesting to note that in case of such systems, the transition from the chelate with a completely deprotonated form to that with a partially deprotonated ligand form is also observed; the above mentioned transition can be realized simply by pH decrease in the gelatin layer.



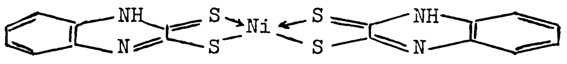
(18)

(Z″ is a double-deprotonated group).

In case of $Ni_2[Fe(CN)_6]$-2,3-quinoxalinedithiol system, the pink color of the thin chelate-containing gelatin layer is changed for the green one, and such color change is accompanied by the shift of absorption maximum from 520 nm up to 630 nm and the emergence of one more band at 700 nm assignable to 1 : 2 chelate.[7] Processing of the gelatin layer containing a cyan chelate results in the reduction of the pink color. In $Ni_2[Fe(CN)_6]$-dithiooxamide system, similar change of colors is observed (from pink-violet into blue) which is accompanied by the bathochromic shift of absorption maximum from 560 nm to 640 nm, but compared to the previously mentioned system, the color change here is found out to be irreversible.[8] The main cause of such differences lies in the structure dissimilarity of "acid" chelates: in case of dithiooxamide, the structure is polymeric **III**, while in 2,3-quinoxalinedithiol it is monomeric **IV**, since steric effects prevent polymer formation. Proton splitting out of the "stiff" polymer structure **III** turns out to be rather difficult and is not observed even at high pH values.

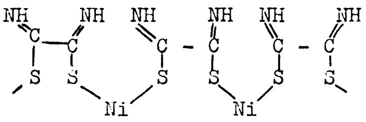


(III)



(IV)

In the $Ni_2[Fe(CN)_6]$-dithiooxamide system, at high hexacyanoferrate(II) and ligand concentrations, insoluble 1 : 1 chelate complex **V** is also formed having a double-deprotonated ligand form which is uncapable of proton addition; this is associated with the characteristics of a coordination polymer.



(V)

Summarizing the above considerations, it should be noted that testing performed with non-silver images containing metallorganic dyes obtained by heterogenous complexing described in this paper, showed that alongside with silver removal and good storability of images, an increase in photographic sensitivity can also be obtained. In a number of cases (such as in the formation of Co(III) dithiooxamide complexes, the sensitivity increase is an order of magnitude greater than the initial value for the silver photographic image, which is of great practical importance. The process described here can also be used for mono- and polychromatic dyeing of silver images and, in particular, for the production of the "blue slides".[9–11] In the near future, the process can be used in the development of a basically new technique of color photography for obtaining "nonageing" images.

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