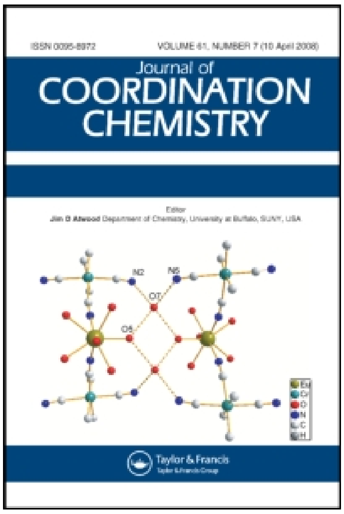

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COORDINATION COMPOUNDS AS COMPONENTS OF SILVERLESS PHOTOGRAPHIC SYSTEMS

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Review

COORDINATION COMPOUNDS AS COMPONENTS OF SILVERLESS PHOTOGRAPHIC SYSTEMS

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Data on the use of 3d- and 4d-element coordination compounds with nitrogen-, oxygen- and sulphur-containing ligands as carriers for silverless photographic images, as active sources of photographic systems, as materials for the formation of silver halide images, as well as their role in the colour diffusion transfer process, have been summarized. The review covers the period 1970–1996.

Keywords: Review; coordination complexes; silverless photography

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1. INTRODUCTION

Modern coordination chemistry shows a trend towards continuous broadening of the range of practical applications of coordination compounds. One of the possibilities for the utilization of coordination compounds is in the photochemical industry where effective reduction in the consumption of expensive raw materials such as silver (or even its full substitution for other cheaper and less scarce substances) is still a most urgent task.[1] In general, saving of silver can be attained by two ways, either by using these agents as radiation-sensitive components of photographic systems or as "working materials" (so-called carriers) for the formation of photographic images on conventional silver halide (AgHal) light-sensitive materials. It should be noted that the second method is widely practised in the silver recovery process when, along with silver compounds, dyes with intense absorption in the visible spectrum region are formed. These dyes are responsible for the formation of silverless photographic images.[2] The most famous system of this type is a colour AgHal photographic material[2,3] where nitorgen-containing organic dyes are the carriers of a photographic image. However, these dyes are rather unstable towards light and aggressive atmospheric attack. As a result, images tend to fade in time.[4] In contrast to these compounds, dyes based on metal–chelates of 3d-elements with nitrogen-, nitrogen–oxygen- and nitrogen–sulphur-containing ligands are more advantageous. For this reason, they are extremely promising carriers of silverless images regardless of whether they are applied with silver halide or as silverless photographic materials.

By now extensive experimental data have accumulated on the employment of chelate coordination compounds of d-elements both as light-sensitive components of photographic layers and as carriers of silverless images in AgHal photographic materials. In our opinion, this new application deserves special discussion. In general, three possible ways of using coordination compounds can be distinguished:

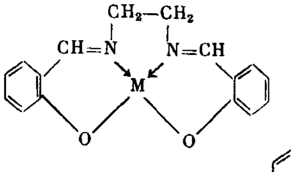
1: as an active source for photographic systems;
2: as a "working material" for the formation of silverless images on AgHal photographic materials employing a conventional processing scheme, *i.e.*, development plus fixing;
3: as colour couplers in diffusion transfer processes.

Thus, the aim of the present review is to assess the prospects for the future employment of coordination compounds in this specific field.

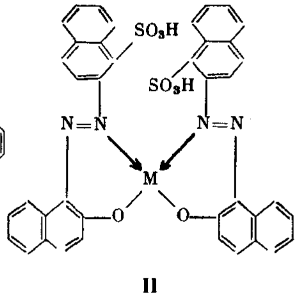
2. CHELATE COORDINATION COMPOUNDS AS ACTIVE SOURCES FOR PHOTOGRAPHIC SYSTEMS

The first use of chelate complexes as light-sensitive agents was by Döbereiner in 1831, long before the era of silver halide photography. He observed the relatively high sensitivity of a Fe(III) complex with oxalate, $[Fe(C_2O_4)_3]^{3-}$, to the blue–violet region of the visible spectrum. In 1842 Hurshell invented cyanotypy, or a blue printing process, a special method of information recording where iron(III) hexacyanoferrate(II) was used as a carrier of a silverless image. This method was used for making copies until the 1960s. Today cyanotypy has been completely replaced by more sophisticated methods and is only of historical interest. However, the search for new systems as sensitive to visible and other types of radiation as AgHal has assumed ever greater importance due to a shortage of silver and the continuous rise in its price.[1] Therefore, particular attention has been paid to a series of chelate complexes as potential competitors of AgHal systems.

As agents suitable for recording UV and visible radiation, quite a wide range of d-element coordination compounds with (N, O)- and (N, S)-ligands, especially azo dyes having formulae I and II[5–9] where M is a 3d-element ion, 8-oxyquinoline, antraquinone and their derivatives[10] have been examined. Various substituted dithizones and dithiocarbaminic acids III and IV where M = Mn, Fe, Co, Ni, Cu, Pd; R^1, R^2 = aryl, alkyl[11–13], and compound V having a similar structure (R, R^1, R^2 = H, alkyl, NO_2, Hal, asymmetric aminogroup, M = Ni)[14]



I



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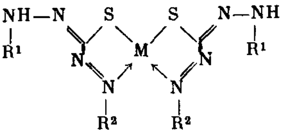

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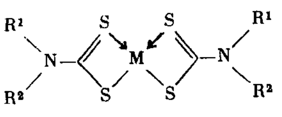
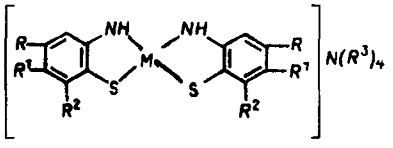
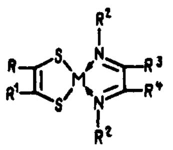


IV



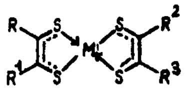
V

as well as a number of dithiolate complexes,[15–20] for example, compounds **VI–VIII**, were suggested as possible useful materials.



VI

(M = Ni, R^1 to R^4 = alkyl, aryl)



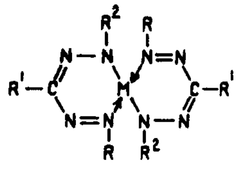
VII

(M = Ni, R^1 to R^3 = unsubstituted C$_1$- C$_{10}$ alkyl, aryl)

VIII

(M = V, Ni, Cu, Rh, R = Ph, Hal, aryl, alkoxyl)

However, greater attention was drawn to chelates with (N, N)-ligands[21–48] among which Zn(II), Co(II) and Hg(II) complexes with benzoindolospiranes,[21] Cu(II) complexes with 1,2-ethylenediamine and analogues having composition $\mathrm{CuL}_n(\mathrm{BR}_4)_2$ where L is a ligand, $n = 2–4$, R is $\mathrm{C}_6–\mathrm{C}_{12}$ aryl[22,23] and compounds represented by general formula **IX** (M = Mn, Co, Ni, Cu, Pd, R–R^2 = H, Hal, OH, COOH, alkyl, aryl, alkenyl, alkoxyl),[28] could be distinguished.

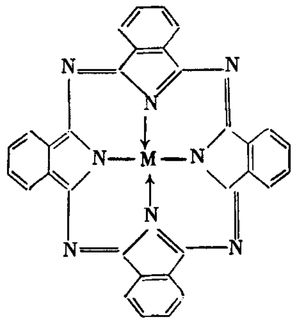


IX

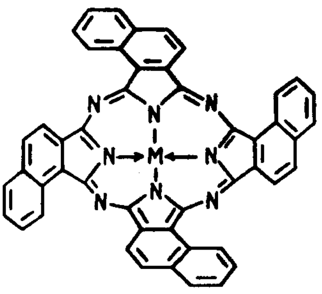
Greatest interest was displayed in chelates of phthalocyanines and their derivatives, the simplest of which could be represented by formula **X**. Originally, phthalocyanine complexes **X** (M = Ni, Cu) were employed as carriers for silverless photographic images[29] whereas chelates of a $[\mathrm{PdL}_m\mathrm{X}_k]\mathrm{L}_k$ type were used as light-sensitive compounds (L is a "space-hampered" polydentate ligand of the 1,1,7,7-tetraethyldiethylenetriamine type; X is Cl, Br, N_3, SCN, Y is X or $\mathrm{B(OR)}_4$ (R is alkyl), $m, n = 1, 2$, $(m + n) = 2–4$, $k, l = 1–4$); colourless phthalocyanine complexes acted as developing agents.

However, a number of new reports over the last few years concern phthalocyanine compounds used as radiation sensors.[30–45] For instance, Mn(III) and VO(II) aklylphthalocyanines were proposed for information recording with the use of a semiconductor laser,[30] 1,2-naphthalocyanines **XI** were employed in optical recording materials[31,35] and fluorine-alkylphthalocyanines were used for recording laser radiation.[36] The use of compounds with ligands similar to phthalocyanines, such as Cu(II), Co(II) and Ni(II) complexes with substituted tetrapyraxineporphyrines[46,47] and Pd(II) complexes with hydroxyflorines **XII** (R = alkyl) was also described.[48]

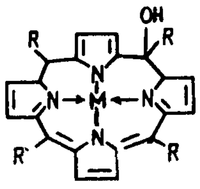
There are plenty of examples of successful employment of d-element coordination compounds with oxyacids as well as with other (O, O)-ligands, in particular with α-diketones and crown ethers,[49–59] for the above-mentioned purposes. A typical example can be represented by formula **XIII**.



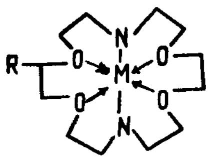
X



XI



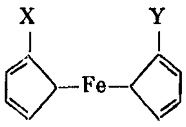
XII



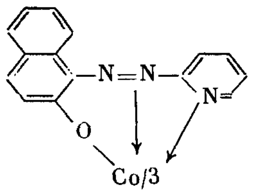
XIII

There are also data on the relatively high sensitivity of carbonyl and cyanide complexes to UV and visible radiation[59–64] and their practical use as active sources in photochromic systems.[65,66] It is interesting to note the use of ferrocene and its derivatives **XIV** for similar purposes,[67–72] including its interactions with the salts of quaternary heterocyclic bases.[67] Chelates of type **XIV**[70] (X, Y is a CO(CH=CH)$_n$Z group, $n = 1, 2$, Z is a substituted or unsubstituted phenyl group) enable preparation of photographic layers recording radiation in the blue–green region. In some silverless systems based on a Ti(IV) chelate with 8-oxyquinoline,[10] a comparatively high sensitivity to the entire visible region (400–700 nm) was obtained, which, however, could not match the sensitivity observed for AgHal photographic materials. It should be noted that in the majority of cases, chelate complexes studied are sensitive to UV radiation and the blue spectrum region only (400–430 nm); the lowest level of radiation absorbed per photolayer surface unit is about $10^{-3}\,\mathrm{J\,cm^{-2}}$ whereas for AgHal photographic layers this parameter is about $10^{-7}\,\mathrm{J\,cm^{-2}}$.[73] In this respect, data on the possible use of chelate complexes for recording fast electron beams, X-rays and other high energy radiations are more optimistic.[74–87] For this purpose, the abovementioned cyclopentadienyl complexes of type **XIV**[76] as well as similar Ni(II), Co(II), Cr(III) and Ti(IV) compounds were used, which enabled the recording of electron beams and X-ray radiation with an energy of up to 20 keV.

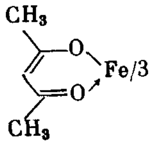
Even more interesting data are presented by other workers[79,85,87] describing Co(III) chelates with ligands being derivatives of 1-(2-pyridylazo)-2-naphthol, **XV**,



XIV



XV



XVI

each of which exceeds silver halide in sensitivity to X-ray radiation. It should be noted that a copper(II) analogue of **XV** with a metal ion/ligand ratio of 1 : 2 has a rather high sensitivity to electron beams.[81] Co(III) complexes with other tetradentate ligands such as 1-(2-pyridyl, 2-thiazolyl, 2-oxazolyl)formazans, and 1-(2-pyridil-2-quinolinyl)dithiooxamide may be used as base materials for light-sensitive systems.[78] A comparatively high sensitivity to X-ray radiation was discovered for a Fe(III) chelate with acetylacetone **XVI**.[77] This complex can be employed for recording high intensity light, such as a laser beam. In future, the list of d-element chelates having similar useful properties may be considerably increased. Investigations in this specific field will attract greater importance in view of the fact that silver halide photographic materials with rather high silver coverage are used for recording hard ionizing radiation in medical and industrial radiography.[88]

Unfortunately, the literature available does not cover in detail the mechanism of silverless image formation in light-sensitive systems containing chelate coordination compounds. A few exceptions can be found.[34,54,71,89–91] The first studied the mechanism of image formation in photographic layers comprising polysilanes and titanyl(IV) phthalocyanine exposed to UV radiation. The decolouration of blue photographic layers occurs as a result of the chemical destruction of titanyl(IV) phthalocyanine initiated by the decomposition of organic polysilane with the formation of free radicals. The processes of photocolouration and photodecolouration of Ti(IV) complexes with oxyacids exposed to UV and γ-radiation have been investigated;[54] in the author's opinion, photochromism is connected with a redox process, according to (2.1).

$$[Ti(C_2O_4)_4]^{4-} + e^- \longrightarrow [Ti(C_2O_4)_3]^{3-} + C_2O_4^{2-} \tag{2.1}$$

This is supported by the fact that a photochrome solution loses its colour not only in the dark but also during oxidation by atmospheric oxygen.[54] Of special interest is the work[90] dwelling upon the mechanism of radiation absorption by Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) complexes with azo dyes (particularly, with 2-oxyphenylazo-2-naphthol and 2-carboxy-4-methyl-phenylazo-4,5-diphenyldiazol) and establishing the ability of the above compounds for radiation recording and light-assisted formation of singlet oxygen. Related work[71] also deserves special discussion. This deals with the process of image formation in ferrocene-based photographic layers and the effect of image reversal influenced by small amounts of compounds being excellent complexing agents for Fe(II) and Fe(III). A supposition has been made that by linking Fe(II) and Fe(III) into respective complexes, such agents exclude them from the autocatalytic process of ferrocene reduction and, in fact, act as inhibitors; their rather high concentrations (for instance, $\sim 0.003\,\mathrm{mol\,dm^{-3}}$ in case of 1,10-phenanthroline) result in complete inhibition of the development process. An attempt has been made[91] to explain the light-sensitive properties of *tris*(2,2-dipyridyl)ruthenium(II) in photoinduced film templates obtained from organic pigments. As can be concluded from the above discussion, the investigations of the mechanism of image formation on silverless light-sensitive materials are extremely specific. A fortunate exception to this is found in work[89] where photographic systems with Cu(I) and Co(III) "active sources" have been considered. In some cases, schemes of the supposed image formation reactions for the respective silverless photographic materials have been presented.

While analysing photographic characteristics of silverless chelate-based photographic systems, it should be noted these systems need further research, especially their sensitization in modern silver halide photographic materials.[2] Therefore, the true potential of these system remains unknown. In view of this, it is appropriate to recall that the lowest radiation level for unsensitized AgHal photographic layers is about $10^{-3}\,\mathrm{J\,cm^{-2}}$, *i.e.*, practically the same as that for chelate-based photographic systems. Other potentialities are still indistinct. The photolysis of chelate complexes and the mechanism of catalytic centre formation (in the vicinity of which a development reaction[2,3] proceeds, accompanied by the formation of a photographic image carrier) still need detailed study. It is regretful that data available have been presented in the patent literature and are of expressed pragmatic character. Apart from that, over the last few years there has been a certain drop in interest concerning chelate-based silverless photographic systems, despite the situation in the world silver market. This phenomenon can be connected with the appearance in the market of so-called "low silver" AgHal photographic materials containing silver with a higher covering power that is responsible for photographic image formation.

3. COORDINATION COMPOUNDS OF 3d-ELEMENTS AS WORKING MATERIALS FOR THE FORMATION OF SILVERLESS PHOTOGRAPHIC IMAGES

Progress made in the research and development of chelate-based silverless photographic systems shows that it is still problematic that such systems will capture a greater market share in the near future. Therefore, the most pressing aim would be to produce high quality silverless images from 3d-element chelates with the employment of modern photographic materials and silver halides. In the latter case, exceptional academic interest is supplemented by significant practical purposes. An image formed on AgHal contains up to 30% of silver remaining upon exposure and standard photochemical processing. Therefore, the substitution of a silver image for a silverless one would effect a considerable saving of silver in the photochemical industry.

Much work has been devoted to the problem of obtaining silverless images from chelate complexes of 3d-elements with (N, O), (N, S), (O, S) and (S, S) ligands.[92–155] A general approach towards the synthesis of silverless images of the above type can be found in reviews.[92,93] This method comprises three-stage processing of a silver image that has previously been formed on an AgHal photographic material by means of a standard procedure.[3] The first stage consists of the processing of a photographic layer with a silver image in an aqueous solution containing $K_3[Fe(CN)_6]$, an oxyacid (usually citric, oxalic or tartaric acid) and a water-soluble salt of Fe(III), Co(II), Ni(II) or Cu(II), such as the chloride or sulphate. As a result of this reaction, elemental silver is oxidized and transformed into a water-insoluble silver(I) hexacyanoferrate(II) with co-precipitation of the hexacyanoferrate(II) of the respective metal contained in the processing solution. Then, the bleached image is processed in aqueous sodium thiosulphate selectively linking an insoluble silver salt to a comparatively water-soluble complex. As a result, only hexacyanoferrate(II) remains in the layer.[93] Finally, the third stage involves the processing of 3d-element hexacyanoferrates(II) in an alkaline solution of a chelating ligand at pH > 9 and a chelate coordination compound is formed in the photographic layer. From the chemical view point, such a reaction is nothing but a complexing process occurring on (3d-metal) hexacyanoferrate(II) gelatin-immobilized matrices as has been described in detail in a number of cases.[115,137,154–156] Quantitatively, the process of metal–chelate silverless image formation proceeding at the third stage may be described either by $D^{\blacktriangledown} = f(\lg H)$ or $D^{\blacktriangledown} = f(D^{\mathrm{Ag}})$ relationships[96–103,121–128,130,139–144,149–151] and by $D^{\blacktriangledown} = f(C_{\mathrm{F}}, C_{\mathrm{L}}^{\mathrm{o}}, t)$ relationships (especially at $[C_{\mathrm{F}} = \mathrm{const}$, varied $C_{\mathrm{L}}^{\mathrm{o}}, t])$;[113,115,116,118,137,138,153,155,156] $D^{\blacktriangledown}$ is the optical density of a metal–chelate image obtained by the three-stage process from the initial silver image with a D^{Ag} density by means of standard development and fixing operations,[2] H is the exposure level providing for the formation of the silver image with a D^{Ag} density, C_{F} is the concentration of the respective (3d-metal) hexacyanoferrate(II) in the photographic layer obtained upon processing of the silver image with a D^{Ag} density and $C_{\mathrm{L}}^{\mathrm{o}}$ is the ligand concentration in the solution used for the third processing stage; t is the time of third stage. Examples of such dependences are shown in Figure 1. Theoretical description of the kinetics of complexing processes and the procedure for performing mathematical analysis of experimental $D^{\blacktriangledown} = f(C_{\mathrm{F}}, C_{\mathrm{L}}^{\mathrm{o}}, t)$ relationships for estimating stoichiometric factors of complexing processes and reaction rate constants are available.[156,157]

More than 30 chelates of Fe(II, III), Co(II, III), Ni(II) and Cu(II) complexes have been tested for the preparation of silverless photographic images on AgHal materials.[94–155] Considerable interest displayed by investigators can be explained by advantageous features such as easy formation in gelatin layers, high absorption intensity in the visible region and relatively high thermodynamic stability. In the majority of cases, metal–chelate image formation proceeds in a rather complicated way and, depending on concentration/time factors, the composition of the silverless image can vary to a considerable extent.[110,111,135,148] However, in a number of cases, especially in hexacyanoferrate(II) nickel(II)-8-mercaptoquinoline and its 5-substituted systems,[112] in hexacyanoferrate(II) nickel(II)-*N*,*N*′-diphenyldithiooxamide,[100,110,111] hexacyanoferrate(II) iron(III)-isonitrosoacetone[150] and hexacyanoferrate(II) iron(III)-8-mercaptoquinoline,[151] the formation of a single complex with metal ion/ligand ratios of 1 : 2, 1 : 2, 1 : 2 and 1 : 3, respectively, was observed.

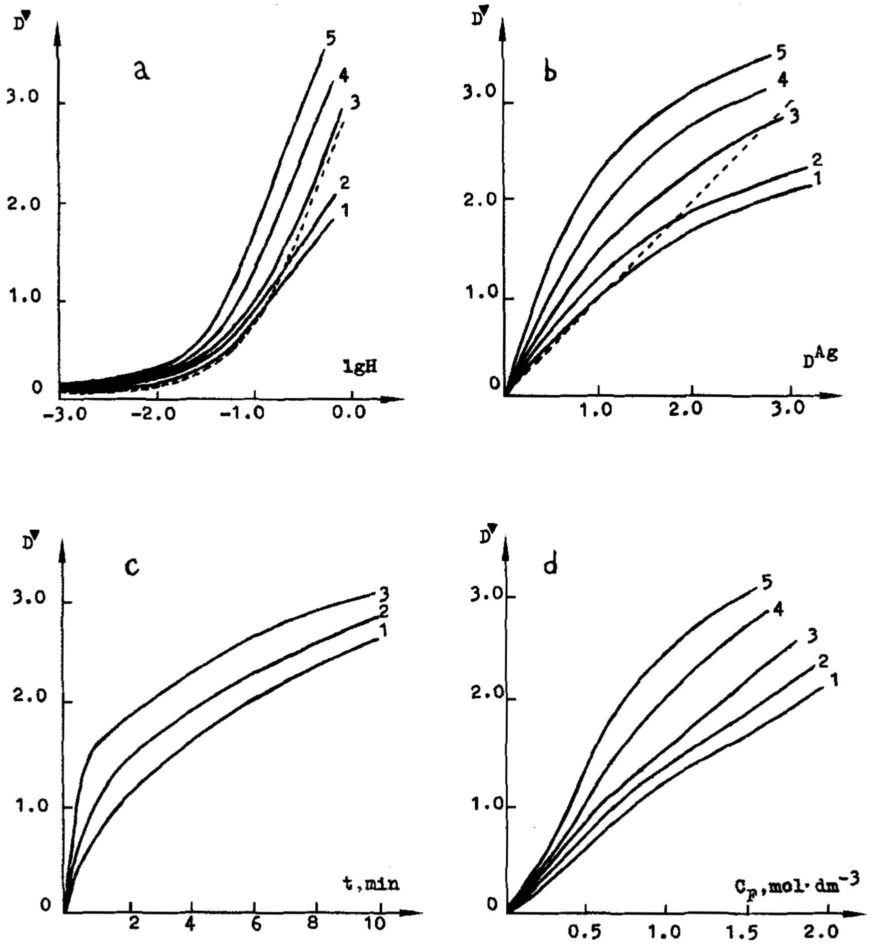
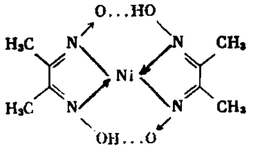


FIGURE 1 Examples of dependences characterizing formation of metal–chelate photographic images consisting of Ni(II) coordination compounds with dimethylglyoxime: (a) $D^{\blacktriangledown}=f(\lg H)$ relationships at fixed ($2.0\times10^{-1}\,\mathrm{mol\,dm^{-3}}$) concentration of ligand in the toning solution. With toning durations 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5); (b) $D^{\blacktriangledown}=f(D^{\mathrm{Ag}})$ relationships at fixed ($2.0\times10^{-1}\,\mathrm{mol\,dm^{-3}}$) concentration of ligand in the toning solution, with toning durations 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5); (c) $D^{\blacktriangledown}=f(C_{\mathrm{F}},C_{\mathrm{L}}^{\circ},t)$ relationships in the coordinate section [$C_{\mathrm{L}}^{\circ}=\mathrm{const}$, varied C_{L}°,t] at $C_{\mathrm{F}}=1.50\,\mathrm{mol\,dm^{-3}}$ for $C_{\mathrm{L}}^{\circ}=2.5\times10^{-2}\,\mathrm{mol\,dm^{-3}}$ (curve 1), $5.0\times10^{-2}\,\mathrm{mol\,dm^{-3}}$ (2) and $2.0\times10^{-1}\,\mathrm{mol\,dm^{-3}}$ (3); (d) $D^{\blacktriangledown}=f(C_{\mathrm{F}},C_{\mathrm{L}}^{\circ},t)$ relationships in coordinate section [$C_{\mathrm{L}}^{\circ}=\mathrm{const}$, varied t, C_{F}] at $C_{\mathrm{L}}^{\circ}=2.0\times10^{-1}\,\mathrm{mol\,dm^{-3}}$ for $t=1$ min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5). The temperature was 20.0 ± 0.5°C. The optical densities of images were measured with a green filter with transmission maximum at 540 nm. The dashed curves on Figure (a) and (b) are the relationships for the initial silver image.

3.1. Silverless Images Consisting of Ni(II) Chelates

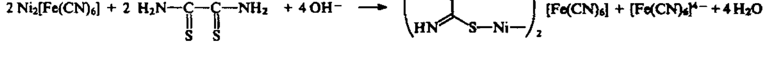
Ni(II) chelates are mentioned most frequently as possible carriers of metal–chelate images.[94–119] The best known chelate used for creating a silverless photographic image is *bis*(dimethyldioximato)nickel(II), **XVII.**[158] The synthesis of images based on such a carrier has been described.[92,93,96]



XVII

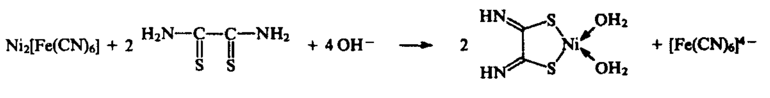
The works cited point out that $D^{\mathrm{v}}=f(D^{\mathrm{Ag}})$ formation curves have a monotonous character without extremes, and with an increase in both $C_{\mathrm{L}}^{\mathrm{o}}$ and t at a fixed D^{Ag} value (and C_{F}, correspondingly) optical densities of silverless images composed of the above compound are observed to tend to limiting values. These images are usually red-pink and are of certain practical interest because when such images are examined in green light (to which the human eye is most sensitive), a considerable increase in optical density compared to the original silver image is observed.

The formation of silverless images based on Ni(II) chelates with dithiooxamide $H_2N{-}C({=}S){-}C({=}S){-}NH_2$ has been given a most detailed study due to the peculiarities of complexing reactions and the variety of coordination compounds formed.[92,93,95,102,103,110,111,113–115] One of the earlier works[95] points out that the formation of images can successfully be employed for the manufacturing of blue slides. Such a possibility was studied in detail.[102,103,110] In the author's opinion, the manufacturing of blue slides composed of Ni(II) chelates with dithiooxamide is less labour-consuming and less environmentally critical in comparison with conventional blue silde production with the use of organic dyes.[159] A detailed analysis of the interaction of Ni(II) hexacyanoferrate(II) formed in the photographic layer upon the first two processing stages with dithiooxamide solutions at pH = 12 shows the formation of five different complex forms **XVIII–XXII** which may be described by Eqs. (3.1)–(3.5).[110,111,113–115,155]

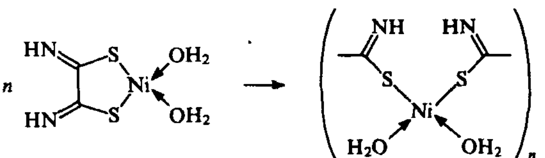


(3.1)

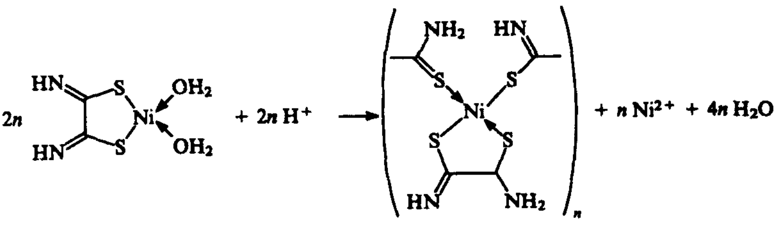
XVIII


XIX

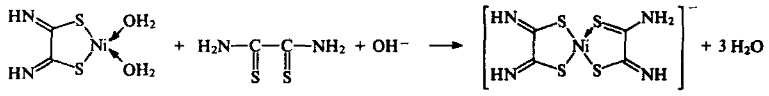
(3.2)


XIX **XX**

(3.3)

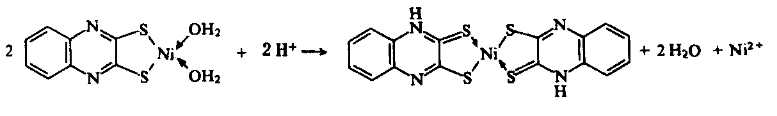

XIX **XXI**

(3.4)


XIX **XXII**

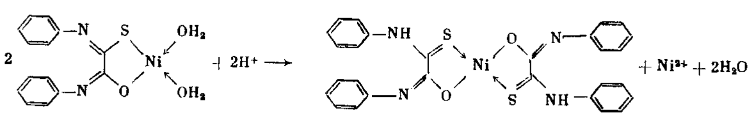
(3.5)

Water-insoluble compounds **XVIII–XXI** render a photographic layer greenish-blue with a grey tint ($\lambda_{max} = 590$–$610\,nm$), pink-violet ($\lambda_{max} = 580\,nm$), violet ($\lambda_{max} = 570\,nm$) and ultramarine ($\lambda_{max} = 640\,nm$), respectively, whereas **XXII** being water-soluble, easily diffuses from photographic layer to a contacting ligand solution. It should be noted that complex **XXII**, on the one hand, makes a positive contribution to the formation of silverless images based on Ni(II) chelates with dithiooxamide at relatively high ligand concentrations ($\sim 8.0 \times 10^{-3}\,mol\,dm^{-3}$ and higher) when the above process is accompanied by a decrease in fog density, in contrast with all known methods of photographic image amplification. On the other hand, a silverless image is not formed at all at extremely high dithiooxamide concentrations in solution ($> 10^{-1}$ mol dm^{-3}).[110] Taking into account a set of processes (3.1–3.5), one can easily explain the peculiar character of $D^{\blacktriangledown}=f(C_F, C^{o}_{L}, t)$ curves $C_F = \text{const}, \text{varied}$ $C^{o}_{L}, t]$ at $C^{o}_{L} > 8.0 \times 10^{-3}$ mol dm^{-3} when with an increase in t; $D^{\blacktriangledown}$ values are observed to grow, reach a maximum and, finally, drop.[92,93,110,111] As can be seen from Eq. (3.1)–(3.5), the transformation of coordination compounds **XIX–XXI** with a change in the photographic layer colour (from pink-violet to ultramarine) is possible in acid medium which is the final stage of the production process for blue slides.[95,107,110,111] It is noteworthy that none of the complexing processes in the Ni(II)-dithiooxamide system either in solution or in solid phase has been recorded so far.[113,114] A similar situation has also been observed for the formation of silverless images based on Ni(II) chelates with quinoxaline-2,3-dithiol[98,110,118] and *N,N′*-diphenylthiooxamide, $C_6H_5NH\text{-}C(=S)\text{-}C(=O)\text{-}NHC_6H_5$,[100,109,116] where the transformation of chelates with a fully deprotonated ligand into those with a partially deprotonated ligand also takes place. This process is accompanied by a sharp change in the colour of the photographic layer.[110,116,118]



(3.6)

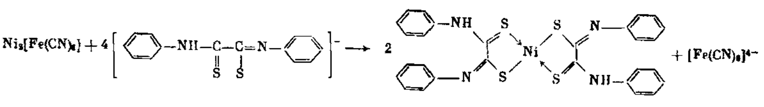
XXIII (pink) **XXIV** (cyan)



(3.7)

XXV (bright yellow) **XXVI** (brown)

It is noteworthy that in contrast with (3.4), similar processes (3.6) and (3.7) are reversible and the original colours of the photographic layer containing **XXIV** and **XXVI** are immediately reduced upon processing in alkaline solutions at pH > 9.[116,118] Such a difference has been explained[116,117] by the fact that in the case of dithiooxamide, a chelate having a nickel(II) – singly deprotonated ligand ratio of 1 : 2 is a coordination polymer whereas in case of quinoxaline-2,3-dithiol and *N,N′*-diphenylthiooxamide, the above compounds are monomers since steric hindrance in these two ligands prevent the formation of polymeric structures. It should also be pointed out that in case of the formation of silverless images based on Ni(II) chelates with *N,N′*-diphenyldithiooxamide, $C_6H_5NH\text{-}C(=S)\text{-}C(=S)\text{-}NHC_6H_5$, processes similar to (3.8)–(3.12) do not occur. The formation of chelate **XXVII** only with a ratio 1 : 2 is observed, according to Eq. (3.8).[99,116]

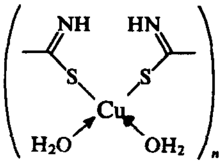

(3.8)

XXVII

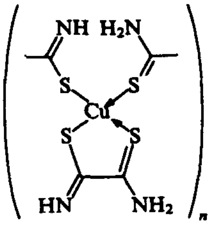
This difference may be caused by both diffusion factors and lower solubility and weaker proton-donor properties of *N*,*N*′-diphenyldithiooxamide,[99,116] compared to dithiooxamide and *N*,*N*′-diphenylthiooxamide. Silverless images obtained from Ni(II) chelates with 8-mercaptoquinoline and some of its 5-substituted derivatives is similar to Ni(II)-*N*,*N*′-diphenyldithiooxamide-based images, expressed by an equation similar to (3.15), have been described.[104,105,112,119] Photographic images obtained from Ni(II) chelates with 8-mercaptoquinoline are characterized by a very steep slope of $D^{\blacktriangledown} = f(D^{Ag})$ curves for low D^{Ag}. This phenomenon may be used in practice for amplifying extremely weak images on radiographic films.[112] A considerable increase in $D^{\blacktriangledown}$ by comparison with initial D^{Ag} values is also observed for silverless photographic images based on Ni(II) chelate with 5-chloro-8-mercaptoquinoline.[119]

3.2. Silverless Images Consisting of Cu(II) Chelates

Cu(II) chelates are less often used for making silverless images than Ni(II) ones.[120–138] However, silverless images obtained from Cu(II) chelates with (N, O), (N, S) and (S, S) ligands are no less interesting than Ni(II) chelates. In the majority of cases, Cu(II) coordination compounds have a much higher absorption in the visible spectrum region than similar Ni(II) complexes. This advantage of Cu(II) chelates makes them highly preferable carriers of photographic images; therefore, the range of copper(II) chelate complexes used for practical purposes is greater by far.[93] As in case of Ni(II), the formation of silverless images based on Cu(II) chelates with dithiooxamide has been studied in more detail.[121,130,137,138] According to results presented in these reports, three water-insoluble compounds, *i.e.*, coordination polymers **XXVIII** and **XXIX** similar to structures **XX** and **XXI**, and a copper(II) hydroxide are formed in a photographic layer containing copper(II) hexacyanoferrate(II) upon processing in an alkaline solution of this ligand.



XXVIII

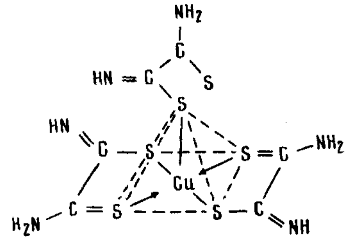


XXIX

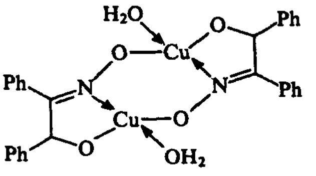
Copper(II) hydroxide appears as a result of the alkaline destruction of $Cu_2[Fe(CN)_6]$ which, unlike nickel(II) hexacyanoferrate(II), can easily be decomposed according to (3.9).

$$Cu_2[Fe(CN)_6] + 4OH^- \longrightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-} \qquad (3.9)$$

However, in case considered, copper(II) hydroxide is accumulated in the gelatin layer of a photographic system only at rather low ($< 10^{-5}\,mol\,dm^{-3}$) ligand concentrations in the processing solution.[138] It is noteworthy that optical densities, $D^{\blacktriangledown}$, of Cu(II) chelate–dithiooxamide-based silverless images increase faster than those of similar Ni(II) chelate images, as can be clearly seen by comparing experimental data.[110,111,130] The formation of a water-soluble Cu(II) dithiooxamide complex with a Cu(II) ion/ligand ration of 1 : 3 is observed at relatively high ligand concentrations ($\sim 1.5 \times 10^{-2}\,mol\,dm^{-3}$) in solution. Structure **XXX** where two dithiooxamide molecules are bidentate and the third molecule is monodentate, has been ascribed to this complex.[137,138] This circumstance must naturally lead to the same results as in case of the formation of Ni(II) chelate–dithiooxamide-based silverless images, particularly to the appearance of peak values on $D^{\blacktriangledown} = f(C_F, C_L^0, t)$ curves [C_F = const, varied C_L^0, t].[137,138] The difference is in the fact that the formation of a soluble Cu(II) complex with dithiooxamide and the simultaneous destruction of a silverless image are displayed at higher concentrations than in the case of Ni(II) chelates. A complex with a similar composition and structure is evidently present during the formation of silverless images based on Cu(II) chelates with quinoxaline-2,3-dithiol,[122,137] which have a yellow-green colour, with a brown tint. These images[122,156] consist of 2 : 2 and 2 : 4 dimeric Cu(II) chelates containing doubly and singly deprotonated ligand forms, respectively. Silverless images obtained from Cu(II) chelates with α-benzoinoxime[123] (where green dimeric chelate **XXXI** is formed),



XXX

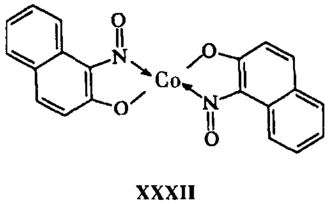


XXXI

8-oxyquinoline,[125] 1,2-dithiocarbamylhydrazine[124] and 1-carbamylhydrazine,[127,137] have also been described in the literature. It should be pointed out that in the last two cases, brown-black silverless images similar to the original silver image are formed. A few reports have been devoted to the investigation of silverless images based on copper(II) chelates with various derivatives of 3-benzoylthiourea, RHN–C(=S)–NH–C(=O)–C_6H_5, where R is a bulky aryl[132–136] and 8-mercaptoquinolines.[129–131] In the majority of cases, these and other Cu(II) chelate images are of “warm” colours affected by both the nature of the chelating ligand and time/concentration factors of the complexing reaction.[155,156]

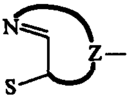
3.3. Silverless Images Consisting of Co(II) and Co(III) Chelates

Co(II) and Co(III) compounds are employed seldom.[139–148] Only two Co(II) compounds have been utilized for obtaining silverless images, *bis*-(2-nitroso-1-naphtholo)cobalt(II), **XXXII**,[139,145,147] and its isomer *bis*-(1-nitroso-2-naphtholo)cobalt(II).[147] Both images are dark red.



XXXII

Co(III) chelates, however, are more preferable carriers of silverless images.[140–144,146,148] A review[146] gives a detailed study of the formation of silverless images based on Co(III) coordination compounds. This work dwells upon quite complicated $D^{\blacktriangledown}=f(D^{\mathrm{Ag}})$ relationships that have been obtained for the formation of silverless images consisting of cobalt(III) complexes with dithiooxamide, *N,N′*-diphenylthiooxamide and *N,N′*-diphyenyldithiooxamide. The peculiar character of $D^{\blacktriangledown}=f(D^{\mathrm{Ag}})$ curves was noted when at any D^{Ag} with an increase in t, D values are observed to grow, reach a maximum, then drop to some minimum and, finally, grow again. The same phenomenon is observed for the formation of silverless images obtained from Co(III) chelates with 8-mercaptoquinoline and its 5-derivatives.[148] In the author's opinion, this may be caused by a stepwise complexing process that can be described by Eqs. (3.10–3.12) where



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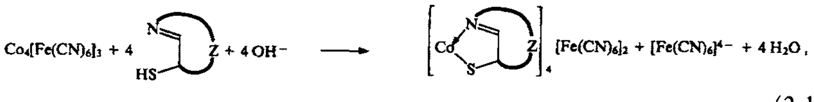
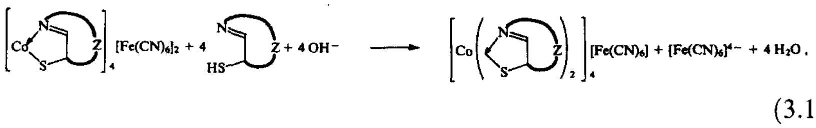
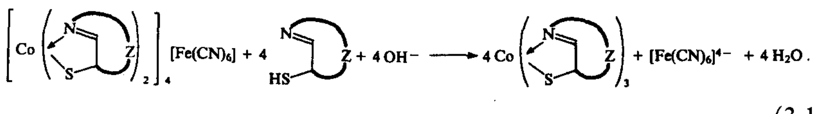


(3.10)



(3.11)

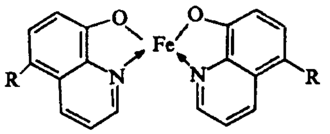


(3.12)

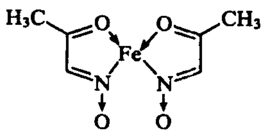
stylized image of the ligand, with Z-open or a closed ring group of atoms. It is noteworthy that a relation of the character of $D^{\blacktriangledown}=f(\lg H)$ and $D^{\blacktriangledown}=f(D^{\mathrm{Ag}})$ curves to the type of photographic material has been employed for constructing the original silver image is observed in the case of the formation of Co(III) chelate–dithiooxamide images, in contrast to those obtained from Ni(II) and Cu(II) chelate with the same ligand. Thus, in the case of radiographic or direct-positive materials, these curves have only one maximum,[140,146] whereas in the case of graphic arts films, two peaks are recorded.[140,144] Such patterns of abovementioned dependences are absolutely unique and have no analogues among processes of silverless image formation from organic and metal–chelate dyes. The cause of this phenomenon has not been explained. Of special note is the fact that the images under study have a very high absorption in the blue region that contributes to a considerable increase (by 30–50 and more) in their sensitivity in comparison with that of the original silver image.[146,148] This phenomenon is of undoubted practical interest.

3.4. Silverless Images Consisting of Fe(II) and Fe(III) Chelates

There are only a few cases using iron(II) or iron(III) chelates for constructing silverless images.[149–154] Nevertheless, ferrous or ferric complexes are preferable and valuable working materials for the formation of silverless photographic images due to their cheapness and availability. Their main disadvantages, however, are, a relatively low absorption in the visible spectrum region and a rather high water solubility which make the number of such chelates used as image carriers quite limited. Only images obtained from Fe(II) complexes with 8-oxyquinoline, **XXXIII**,[149,152,154] isonitrosoacetone, **XXXIV**[150] and Fe(III) chelates with 8-mercaptoquinoline[151] have been reported so far. The most promising ligand for constructing photographic images is 8-oxyquinoline, which when reacts with Fe(II) forms a brown-black compound **XXXIII** rendering the gelatin layer a colour similar to that of the original silver image, though with higher optical densities.[152]

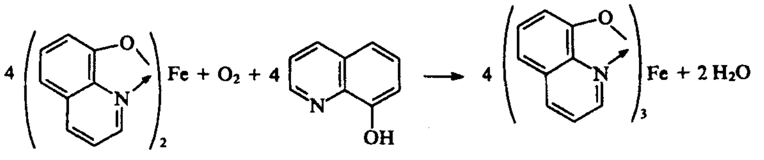


XXXIII



XXXIV

Simultaneous formation of Fe(III) oxyquinoline also takes place during the synthesis of silverless images with the above carrier, which could be explained by the existence of a redox process (3.13).



(3.13)

XXXIII **XXXV**

However, the above reaction is not observed in the formation of blue silverless images composed of iron(II) chelates with isonitrosoacetone.[150]

This reaction plays a decisive role in the formation of silverless images based on iron chelates with 8-mercaptoquinoline where the image carriers are Fe(III) chelates.[151] These orange-red silverless images can be used in practice for amplyifing silver images on silver halide photographic materials.

A specific result of the transformation of a silver image into a 3d-element chelate image, *i.e.*, image amplification or reduction, is considerably dependent both on the nature of the chelate used and the type of photographic material employed in the process. Thus, radiographic materials usually display amplified images in comparison with the original silver image, whereas direct-positive and graphic arts systems show reduced images.[94–101,120–128,139–141] This effect has been explained[124] by the high covering power of image silver for the last two types of photographic materials. Hence, in the case of direct-positive and graphic arts films, lower silver concentrations in the photographic layer account for the same optical density, as compared with that of radiographic materials and, consequently, lower contents of metal hexacyanoferrate(II) co-precipitating with Ag(I) compounds. Certain structural characteristics of silverless images obtained from various chelate complexes, especially their resolution values, have been estimated.[160] According to this estimation, in the majority of cases the above characteristics have little difference from those of the original silver image. This is of principal importance since it enables one to assert potential suitability of these materials for non-destructive inspection purposes, especially in medical radiography. Data on the resolving power of silverless images based on Cu(II) chelates with α-benzoinoxime[160] allow one to hope that images with such a carrier can even be recommended for silverless holographic materials where the most stringent requirements with respect to resolution are specified.[1] It is significant that a drop in the resolving power of silverless images, as compared to the original silver image, is mostly observed in cases when in the course of the complexing reaction a partial destruction of a water-insoluble chelate takes place due to its deprotonation or the addition of ligand molecules which is accompanied by the formation of water-soluble complexes.[160]

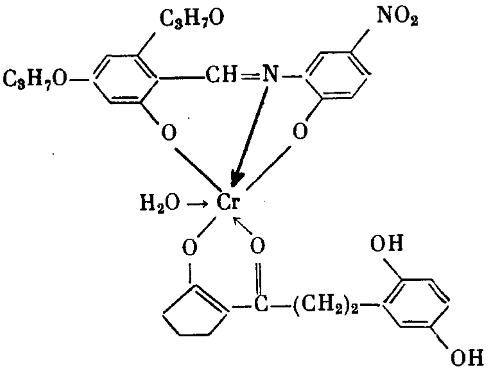
4. CHELATE COMPLEXES IN THE COLOUR PHOTOGRAPHIC PROCESS

In 1947, Land, an American inventor, proposed a single-stage photographic process including the simultaneous photochemical processing of an exposed film and the formation of a positive black-and-white or colour image.

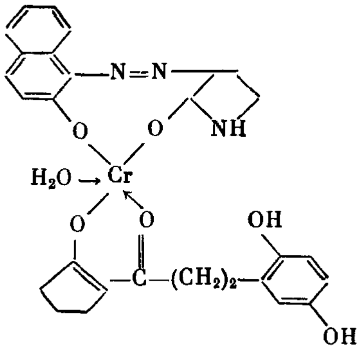
A light-sensitive layer of the exposed photomaterial immediately contacts with a photographic paper containing a special receiving varnish layer. In the course of the photochemical treatment, silver or dye particles creating a negative image on the photographic material remain in the exposed areas. At the same time, the particles in the unexposed areas of the photographic material diffuse into the receiving layer of the photographic paper where a positive image is formed.

A colour photographic material consists of three layers, each of which, in turn, is composed of two intermediate layers. The upper AgHal light-sensitive sublayer has a sensitivity to red, blue and green light whereas the lower intermediate layer contains a colour coupler being a supplement to the colour of the upper sublayer sensitivity (*i.e.*, cyan, yellow and magenta, respectively). A silverless image obtained is composed of the above colour couplers being nothing but intensively coloured 3d-element chelates with various nitrogen, nitrogen–oxygen and nitrogen–sulphur ligands.[161–200] This procedure is called a colour diffusion process and is at present a unique practical case when the photographic material used results in an image entirely consisting of chelate complexes. The structure and properties of such photographic materials have been described in reviews.[169,173]

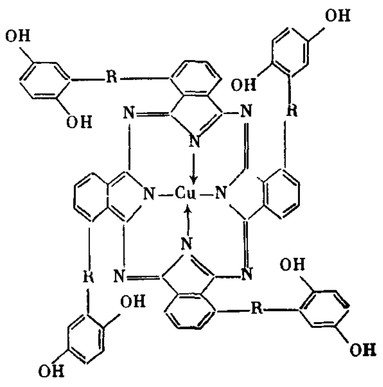
Today the most popular version of the above photographic process is the case where magenta and yellow colour couplers are represented by chromium(III) complexes with azomethines or azo dyes and the cyan coupler is represented by Cu(II) complexes with phthalocyanine or its substituted derivatives.[161–172] Thus, chelate compounds **XXXVI–XXXVIII** have been used[164] where R is $-SO_2NHCH(CH_3)CH_2-$.



XXXVI (Yellow coupler)



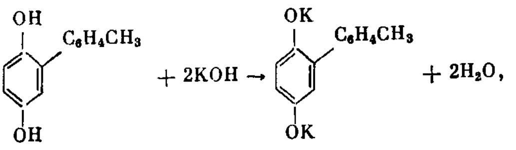
XXXVII (Magenta coupler)



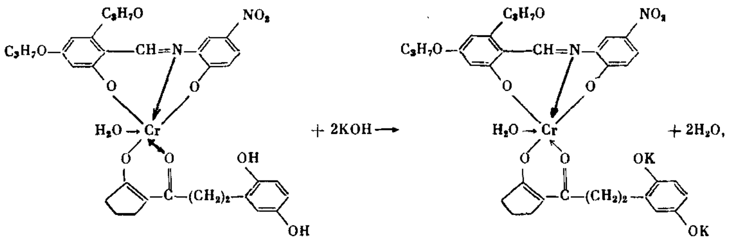
XXXVIII (Cyan coupler)

SX-70 film (Polaroid, USA), a widely known commercial photographic material based on the diffusion transfer process, employs the above or related colour couplers.[168] Obviously, such a combination of chelates is most useful and suitable for the successful formation of a colour image. Other Cr(III) complexes were also proposed, did not become widely practised.

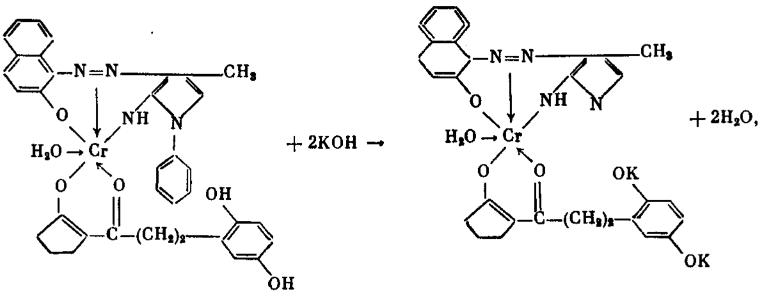
Silverless image formation in the abovementioned systems has been described.[169,173] Compositions used for development comprise an alkali (NaOH or KOH, as a rule) being a compulsory element and an active source of the processing. In the course of development, the alkali diffuses into a light-sensitive layer and ionizes a developing agent (usually, methylphenylhydroquinone) and colour couplers, according to (4.1)–(4.4). As a result, inactive water-insoluble couplers are transformed into active soluble compounds.



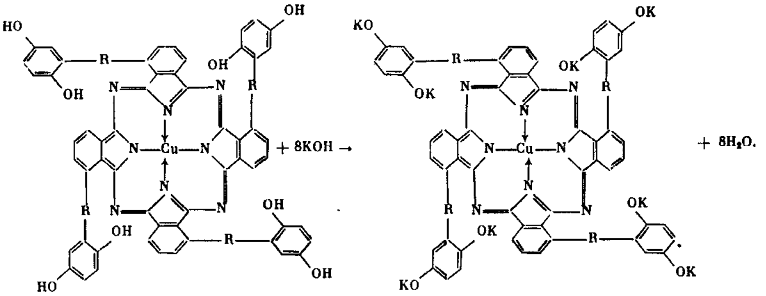
(4.1)



(4.2)

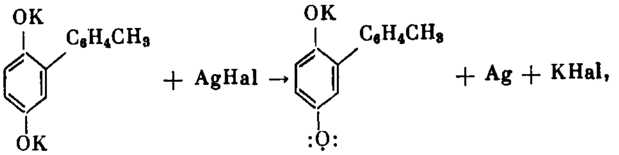


(4.3)



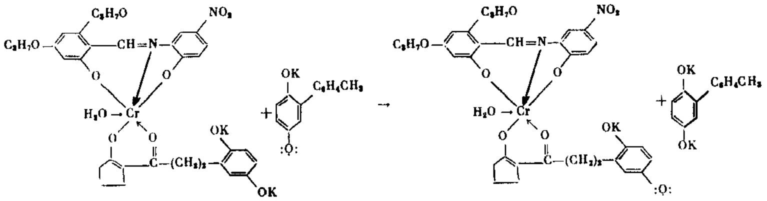
(4.4)

In the exposed areas, potassium or sodium methylphenylhydroquinonate reduces AgHal according to the scheme given below (4.5) and is transformed into a corresponding ion-radical



(4.5)

that further interacts with an ionized form of the coupler and converts it into semiquinone **XXXIX**, in particular, for the yellow coupler, according to (4.6).



(4.6)

Semiquinone **XXXIX** is rather easily transformed into a water-insoluble coupler uncapable of diffusing and contacting with the receiving layer. In the unexposed areas of the photographic material where processes (4.5) and (4.6) are absent, soluble forms of colour couplers **XXXVI–XXXVIII** emerging in the course of reactions (4.2)–(4.4) penetrate the receiving layer and contact with the photographic paper form mono- or polychrome images. Finally, they are converted back into insoluble forms **XXXVI, XXXVII** and **XXXVIII**, respectively.

The above chelate complexes are used in the colour diffusion transfer process most frequently.[163,173] However, silverless images based on other complexes can also be synthesized. Thus, along with Cu(II) phthalocyanine complexes, Co(II) and Ni(II) compounds with the same ligands[182] as well as d-element chelates with β-ketoacetamidoimidazoquinoline having a very high light resistance have been proposed.[184] In recent reports the possibility of using coordination compounds containing Ni(II),[184–188,194,198] Co(III)[191] as well as platinum group metals such as Rh(III)[192] and Pd(II)[186,188,194,200] have also been considered. Theoretically, quite a wide range of suitable chelate complexes with bulky (N,N) and (N,O) ligands can be employed in the colour diffusion transfer process.[192] However, over the last five years the list of chelate complexes used in this process has remained almost unchanged.

5. CONCLUSIONS

The formation of silverless images based on intensively coloured 3d-element chelate complexes, being somewhat exotic today, is of significant interest both for photographic science and the chemistry of coordination compounds. The manufacturing of the above complexes marks the appearance of a new original scientific trend in the field of chemistry, *i.e.*, complexing in metal-containing gelatin-immobilized matrices.[115,137,156] As far as practical significance is concerned, the formation of metal–chelate photographic images, along with silver recovery, is capable of considerably increasing the information value of silver halide light-sensitive materials. The above chelate complexes and processes can also be even more helpful for imaging photography. In future, the creation of new colour photographic processes employing chelate complexes with excellent light and age resistance characteristics might be expected. There is every reason to believe that this problem will be successfully solved.

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