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Complexes of *d* elements with chelate and macrocyclic ligands as promising components of nonsilver photographic systems

O V Mikhailov

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Abstract. Data concerning the most important aspects of the use in the colour photoprocess with diffusional transfer of the image of coordination compounds of *d* elements with nitrogen-, oxygen-, **and sulfur-containing chelate and macrocyclic ligands as the 'working material' or the creation of nonsilver photographic images on silver halide light-sensitive materials by means of their additional treatment and also as the active principle of nonsilver light-sensitive systems are treated systematically and discussed. The bibliography includes 235 references.**

I. Introduction

A current characteristic feature of modern coordination chemistry is a tendency, together with the constant expansion of the range of compounds investigated, to expand also the regions of their practical application. During the last 10 – 15 years, the tendency to employ coordination compounds as components of nonsilver photographic systems has arisen. This will promote the replacement of silver by other less expensive readily available chemical compounds.[1]

In principle, economies can be achieved in the use of silver in two ways: by employing coordination compounds either as 'carriers' of photographic images on traditional silver halide light-sensitive materials or as components of nonsilver photographic systems sensitive to radiation. It is noteworthy that the first procedure has nowadays become quite common in silver recovery processes, during which dyes, intensely absorbing in the visible region of the spectrum, arise on the silver halide materials together with silver compounds. After the removal of silver-containing compounds from the photographic emulsion, these dyes form nonsilver photographic images.[2] The best known dyes of this type are organic dyes containing both nitrogen and oxygen.[2,3] However, the resistance of these dyes to the action of light and corrosive agents in the environment is low, as a result of which the nonsilver photographic images containing them are decolorised comparatively rapidly.[4] Dyes based on metal chelates and especially on the metallomacrocycles of 3*d* elements with nitrogen-, nitrogen and oxygen-, and nitrogen and sulfur-containing ligands are free of this disadvantage. There are grounds for the hypothesis that the latter are extremely promising carriers of nonsilver photographic images regardless of whether they have been formed on nonsilver or even on silver halide light-sensitive materials.

Towards the end of the 1980s, extensive data accumulated on the use of metal chelates and metallomacrocycles of *d* elements as carriers of nonsilver photographic images on AgHal photographic materials and as intrinsic light-sensitive components of photographic emulsions. These results have been surveyed by Mikhailov and Polovnyak.[5] However, during the time elapsed since the publication of this review (almost ten years), quite a few new investigations have been published. Among them, one must differentiate studies devoted to the use of metal chelate and macrocyclic coordination compounds as the 'working material' for the formation of nonsilver images on AgHal photographic materials, as coloured components in silver halide photographic processes with diffusional transfer of the image, and as the 'active principle' of photographic systems.

II. Chelate and macrocyclic coordination compounds as carriers of nonsilver images formed on 'traditional' AgHal photographic materials

It is known [1,2,4] that up to 30% of the silver contained initially in the given photographic material remains in the silver images produced on AgHal photographic materials after their exposure and subsequent chemical-photographic treatment in accordance with the standard scheme (development plus fixation). Thus the replacement of a silver image by a nonsilver one can afford fairly appreciable additional economies in the use of silver in the chemical-photographic industry and it follows therefore that this problem cannot be ignored. The process involving the transformation of a silver image into a nonsilver one using carriers based on azo- and azomethine dyes has long been known. In principle, this process actually makes it possible to extract silver fully from, the treated AgHal photographic material, but the nonsilver images thus obtained are extremely unstable during storage and are readily 'decolorised' by both light and by corrosive agents in the environment.[2] On the other hand, chelate and macrocyclic coordination compounds of *d* elements are very inert in relation to the action of the above factors [6] and one may therefore expect that their employment as carriers of nonsilver photographic images would make it possible to store the image for

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a longer time. This factor stimulated the search for technologies involving the transformation of silver images on AgHal photographic materials which could actually lead to the formation of metal complex nonsilver images. Their essential feature reduces to the following. The elemental silver contained in the initial image is transformed into a mixture of compounds of silver(I) (in particular AgHal) and of some other *d* element on treatment with a specific solution. Next the photographic emulsion containing this kind of 'mixed' image is treated with a solution which converts the silver(I) compound into a water-soluble one, but does not interact with the other component of the 'mixed' image. This results in the formation of a nonsilver photographic image, the carrier of which is the inorganic compound formed previously in the photographic emulsion together with the silver(I) compound. On treatment of the latter with the appropriate solution, specific complex-formation reactions result in the formation of the final metal chelate nonsilver image. The process described usually involves three stages.[5,7]

1. The bleaching of the silver image formed initially on the AgHal photographic material as a result of the standard chemical-photographic treatment (development plus fixation) accompanied by the deposition in the photographic emulsion of the hexacyanoferrate(II) complex of some kind of 3*d* element. These two processes can usually be combined. For this purpose, the photographic emulsion with the silver image is kept in an aqueous solution containing potassium hexacyanoferrate(III), some kind of hydroxy acid (usually citric, oxalic, or tartaric) and (or) its salt, and a soluble salt of the 3*d* ion (usually chloride or sulfate). However, in certain cases such combination is impossible and the bleaching and deposition of the corresponding hexacyanoferrate(II) have to be carried out in two different solutions — this happens, for example, in the case of $Co_2[Fe(CN)_6]$.

2. The fixation of the bleached image, which results in the elimination from the photographic emulsion of the silver(I) compounds formed in the latter after the bleaching stage. This stage is carried out by maintaining the photographic emulsion with the bleached image in an aqueous solution of sodium thiosulfate ($Na_2S_2O_3$).

3. The toning of the image which has passed the above two stages, which results in the formation of the metal chelate nonsilver photographic image. This stage is achieved by maintaining the photographic material in a solution containing some kind of chelating organic compounds and alkaline reagents (usually NaOH, KOH, or Na_2CO_3).

The processes occurring in the first two stages are noncatalytic.[3] As a consequence of this, when they are carried out exhaustively the amount of the hexacyanoferrate(II) of the 3*d* element formed in the photographic emulsion is determined exclusively by the content of silver in the initial photographic image. The third stage is none other than the complex formation reaction in 3*d* metal hexacyanoferrate gelatin-immobilised matrix systems.[8,9] The amount of chelate complex formed depends primarily on the concentration of the hexacyanoferrrate(II) of the corresponding metal ion in the photographic emulsion and the concentration of the chelating compounds in the 'toning' solution in contact with it. It is therefore natural to expect that the third stage is in fact decisive in the formation of the nonsilver image with carriers comprising chelate and macrocyclic coordination compounds. A factor such as the solubility of the complex formed in the toning stage then becomes important: if it exceeds a certain critical level, the leaching of this complex from the photographic emulsion comprising the treated material becomes possible, which leads to some decomposition of the metal chelate nonsilver image itself.

The process involving the formation of images in the third stage can be described quantitatively in terms of the following relations: $D' = f(\lg H)$, $D' = f(D^{Ag})$ or $D' = f(c_F, c_L^0, t)$, where D' is the optical density of the metal chelate image obtained after treatment from the initial silver image with an optical density D^{Ag}, H is the level of exposure ensuring, after carrying out the standard chemical-photographic treatment, the formation of a silver image with a density D^{Ag}, c_F is the concentration of the hexacyanoferrate(II) of the corresponding ion of the 3*d* element in the photographic emulsion attained after bleaching and fixation of the silver image, c_L^0 is the concentration of the ligand in the solution used in the toning stage, and t is the duration of toning.

The theory of the kinetics of the processes occurring under these conditions and the procedure for the mathematical treatment of the experimental $D' = f(c_F, c_L^0, t)$ relations in order to determine the stoichiometric coefficients of the complex formation reactions and their rate constants have been described by the present author.[10]

More than 30 different Fe(II), Fe(III), Co(II), Co(III), Ni(II), and Cu(II) coordination compounds with N,O-, N,S-, and N,O,S-chelate and macrocyclic ligands have now been tested for the production of nonsilver photographic images on AgHal photographic materials.[11–81] The increased attention devoted precisely to the chelates of the above metal ions is linked directly to factors such as the ease of their formation in gelatin emulsions of the AgHal photographic materials, the considerable absorption intensity in the visible part of the spectrum, and a fairly high thermodynamic stability.[12] The carriers for metal chelate nonsilver images mentioned most frequently are Ni(II) chelates,[13–42] to a lesser extent Cu(II) chelates,[43–64] and to a still lesser extent Co(II) and Co(III)[65–75] as well as Fe(II) and Fe(III)[76–81] chelates. In most cases the formation of metal chelate photographic images proceeds in a very complex manner and the composition of the nonsilver image depends on the concentration-time regime (*i.e.* on the specific values of the parameters c_F, c_L^0 and t).[29,30,58,74] However, one should note that in a number of instances, for example in the Ni(II)–8-mercaptoquinoline (or its 5-substituted derivatives),[31,39,40] Ni(II)–*N*,*N*′-diphenyldithiooxamide,[19,29,30] Fe(II)–isonitrosoacetone,[77] and Fe(II)–8-mercaptoquinoline[78] systems, the formation of only one complex species with metal ion : ligand ratios of 1 : 2, 1 : 2, 1 : 2, and 1 : 3 respectively was recorded.

The formation of nonsilver images from chelate and macrocyclic Ni(II) coordination compounds is preceded by the stage involving the bleaching of the silver image with deposition of $Ni_2[Fe(CN)]_6$. In all the cases described in the literature, this stage is carried out using the following composition: 15.0 g $NiCl_2 \cdot 6H_2O$ + 88.0 g Na_3HCt (or K_3HCt) + 14.0 g $K_3[Fe(CN)_6]$ + H_2O (up to 1 litre) [HCt^{3-} is the citrate trianion $^{-}O_2CCH(OH)CH(CO_2^-)CO_2^-$].

The bleaching stage is usually carried out for 20–25 min at 20–25 °C. Nickel hexacyanoferrate is formed by the reaction

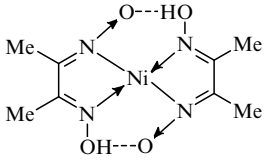
$$6[Ni(HCt)_3]^{7-} + 4[Fe(CN)_6]^{3-} + 4Ag + 4Cl^- \longrightarrow$$
$$\longrightarrow 3Ni_2[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4AgCl + 18\,HCt^{3-}.$$

After the 'bleaching' of the image

$$AgCl + 2\,S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^-$$

only nickel hexacyanoferrate remains in the photographic emulsion imparting a pale yellow-green colour to the latter. By varying further the composition of the toning solution under toning conditions, it is possible to obtain diverse nickel-containing nonsilver photographic images.[11,12]

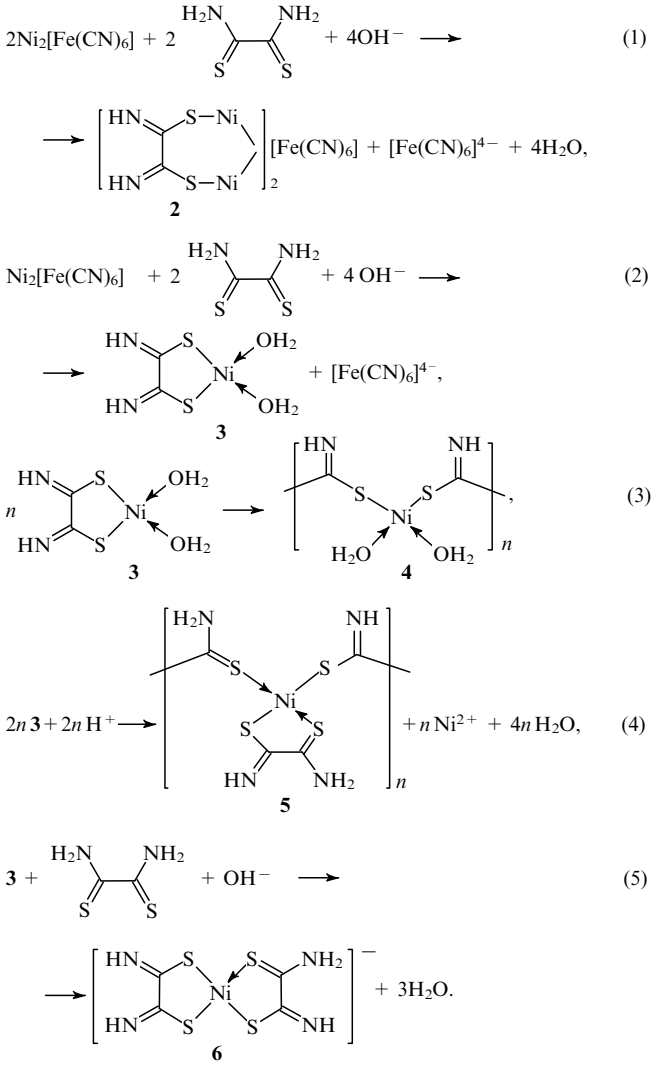
The most familiar coordination compound which may be used to form a nonsilver photographic image on AgHal light-sensitive materials is bis(dimethylglyoximato)nickel(II).[82]



1

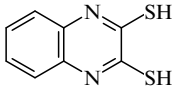
The generation of images with this type of carrier has been described.[11, 12, 15, 16] It was noted that the optical density relations $D' = f(\lg H)$, $D' = f(D^{Ag})$, and $D' = f(c_F, c_L^0\ t)$ put forward above are monotonic, lack extrema, and tend to a limiting value with increase in c_L^0 and t for a fixed value of D^{Ag} (and hence c_F). The nonsilver pink or pink-red images obtained are of particular practical interest because, when they are examined under green light (to which the eye is known to be most sensitive), there is an appreciable increment in the optical densities D compared with the optical densities of the initial silver image D^{Ag}.[15, 16]

The formation of nonsilver images based on Ni(II) chelates comprising dithiooxamide has been investigated in detail because of the extremely interesting colour transitions occurring in this instance and the wide variety of coordination compounds produced.[8, 11, 12, 14, 21, 22, 29, 30, 32–34] On interaction of nickel(II) hexacyanoferrate, formed in the photographic emulsion after the occurrence of stages 1 and 2, solutions of dithiooxamide (pH 12.0) give rise to five different complexes **2**–**6**.[8, 29, 30, 32–34]

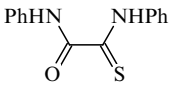


Compounds **2**–**5** are insoluble in water and impart a greenish-blue colour to the photographic emulsion with a grey tint (λ_{max} = 590–610 nm), a pink-violet colour (λ_{max} = 580 nm), a violet colour (λ_{max} = 570 nm), and a dark-blue colour (λ_{max} = 640 nm) respectively, while compound **6**, being insoluble in water, readily diffuses from the photographic emulsion into the toning solution in contact with the latter. A unique and from the practical point of view an extremely valuable property is actually associated with the formation of compound **6**: the process involving the generation of non silver images from nickel(II) chelate complexes of dithiooxamide at fairly high concentrations of the above organic reagent in the toning solution (8.0×10^{-3} M) is not only unaccompanied by an increase in fogging compared with that for the initial silver image but actually entails its diminution. (At dithiooxamide concentration in the toning solution $c_L^0 > 0.1$ M, the nonsilver image is not formed at all.[29]). This factor has been used at one time to increase the sensitivity of direct positive photographic materials.[26] In an early study,[14] it was noted that the process involving the generation of such images may be applied successfully to prepare the so-called blue slides, which have been recently used increasingly for presenting illustrations at conferences, symposia, *etc*. The preparation of 'blue slides' with carriers consisting of nickel(II) chelate complexes of dithiooxamide has been investigated in detail.[21, 22, 29] It has been noted that this process is less laborious and, which is particularly important, its sensitivity to external conditions is much less critical compared with the traditional technology for the preparation of 'blue slides' on the basis of organic dyes, one of the versions of which has been described by Filin *et al*.[83] The fact that the sky-blue or blue metal chelate images obtained in our case have a higher purity of their light lines and a better contrast than those described by Filin *et al*.[83] merits attention in this connection. It is remarkable that none of the processes (1)–(3) in the nickel(II)–dithiooxamide system has been recorded hitherto for complex formation in solution.[32, 33]

Bearing in mind the set of formation reactions of compounds **2**–**6**, it is easy to explain the unusual time variation of the optical densities of the nonsilver image in the third stage: for $c_L^0 > 8.0 \times 10^{-1}$ M, the values of D' initially increase with t, reach a maximum, and then fall.[11, 12, 29, 30] According to Eqn (4), the transition **4** → **5**, entailing a change in the colour of the photographic emulsion from violet to dark-blue, is possible in an acid medium. The concluding stage of the technological process for the preparation of 'blue slides' is associated with this transition.[14, 26, 29, 30] A similar type of $D' = f(D^{Ag})$ and $D' = f(c_F, c_L^0, t)$ relations has also been noted for the processes involving the generation of nonsilver photographic images with carriers consisting of nickel(II) chelate complexes of quinoxaline-2,3-dithiol **7** and *N*,*N*′-diphenylthiooxamide **8**:[19, 28, 35]

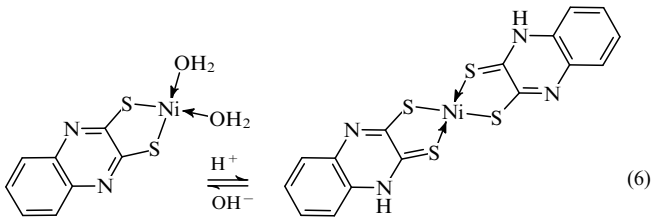


7

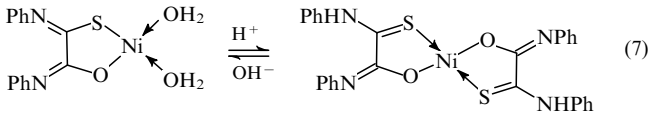


8

Incidentally, here too the transition from chelates with complete deprotonation of the ligands to chelates with partial deprotonation of the latter is also observed, which is accompanied by a sharp alteration in the colour of the metal chelate photographic image (from pink to blue-green in the case of quinoxaline-2,3-dithiol and from bright-yellow to brown in the case of *N*,*N*′-diphenylthiooxamide).[29, 35, 37] It is remarkable that, in contrast to the process in which a dark-blue nonsilver image is generated from the nickel(II) chelate complex of dithiooxamide (the transition **4** → **5**), the analogous processes involving the generation of blue-green and brown images from quinoxaline-2,3-dithiol and *N*,*N*′-diphenylthiooxamide are reversible and, when they are treated with alkaline solutions at pH > 9.0, their initial colour (pink and bright-yellow respectively) is immediately restored [35–37] and a very appreciable decrease (to the extent of 50%–55%) in the optical densities of both the pink and bright-yellow metal chelate images is then observed. Whereas complex **5** is a coordination polymer, the nickel(II) complexes of quinoxaline-2,3-dithiol and *N*,*N*′-diphenylthiooxamide are coordination monomers because steric hindrance in the quinoxaline-2,3-dithiol and *N*,*N*′-diphenylthiooxamide molecules precludes the formation of polymeric compounds. The processes involving the generation of metal chelate images can therefore be described by reactions (6) and (7) in the case of quinoxaline-2,3-dithiol and *N*,*N*′-diphenylthiooxamide.

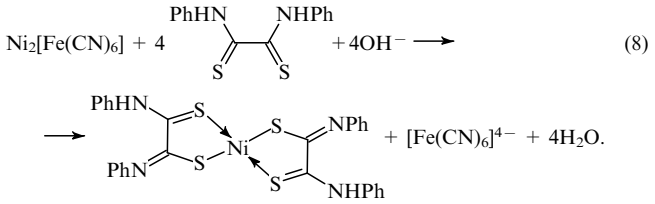


9 (pink) **10** (blue-green) (6)



11 (bright yellow) **12** (brown) (7)

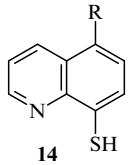
Reactions (1)–(7) do not occur on formation of nonsilver metal chelate images from nickel(II) coordination compounds with a ligand close to dithiooxamide and *N*,*N*′-diphenylthiooxamide — *N*,*N*′-diphenyldithiooxamide PhNHC(S)C(S)NHPh; in this case, this process is described by Eqn (8):[35]



13 (red-violet) (8)

The cause of this difference should be sought both in the influence of diffusion factors and in the poor proton-donating properties and the sparing solubility of *N*,*N*′-diphenyldithiooxamide compared with dithiooxamide and *N*,*N*′-diphenylthiooxamide.

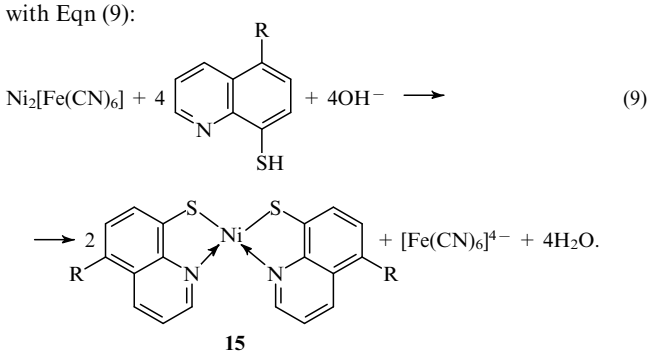
The technology for the generation of nonsilver photographic images from nickel(II) chelate complexes of 8-mercaptoquinoline and a series of 5-substituted derivatives having the general formula **14** has been described.[23, 24, 32, 38–40]



14

R = H, SH, SMe, Cl, Br.

In this case, the nonsilver image is generated in accordance with Eqn (9):



15 (9)

The colour of the images thus obtained varies from pink-red to dark-brown. A very steep slope of the $D' = f(D^{Ag})$ curves in the range of low optical densities of the initial silver image is characteristic of the nickel(II) complexes of unsubstituted 8-mercaptoquinoline. It has been suggested that this factor be used to intensify very weak photographic images on radiographic materials.[31, 39] A very considerable increase in D' compared with D^{Ag} has been noted also for nonsilver metal chelate images based on nickel(II) compounds of 5-chloro-8-mercaptoquinoline.[38, 40]

The nonsilver images derived from copper(II) chelate complexes with N,O-, N,S-, N,O,S-, and S,S-donor ligands are also of interest. Their absorption in the visible region of the spectrum exceeds in most cases the absorption of the analogous nickel(II) chelates. Formally this fact renders copper(II) coordination preferable for the generation of nonsilver metal chelate photographic images compared with those based on nickel(II). This probably accounts for the greater range of copper(II) chelate complexes compared with the nickel(II) complexes.[12]

The formation of metal chelate images is also preceded by the stage in which the initial silver images is bleached and fixed. The bleaching is carried out either in the 7 g $CuSO_4 \cdot 5H_2O$ + 90 g Na_3HCt (or K_3HCt) + 6 g $K_3Fe(CN)_6$ + H_2O (up to 1 litre) solution (see Michailov and Polovnyak [53]) or the 7 g $CuSO_4 \cdot 5H_2O$ + 50 g $K_2C_2O_4$ + 4 g $K_3Fe(CN)_6$ + H_2O (up to 1 litre) solution (see Mikhailov *et al.*[62]).

In both cases, the bleaching process occurs at 20–25 °C for 20 min. The nonsilver image generation processes are described by Eqns (10) and (11):

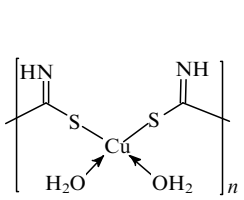
$$6[CuCt_2]^{6-} + 4[Fe(CN)_6]^{3-} + 4Ag + 12H^+ \longrightarrow \quad (10)$$
$$\longrightarrow 3Cu_2[Fe(CN)_6] + Ag_4[Fe(CN)_6] + 12HCt^{3-},$$
$$6[Cu(C_2O_4)_2]^{2-} + 4[Fe(CN)_6]^{3-} + 4Ag \longrightarrow \quad (11)$$
$$\longrightarrow 3Cu_2[Fe(CN)_6] + Ag_4[Fe(CN)_6] + 12C_2O_4^{2-}.$$

In order to fix the 'bleached' image, the treatment of the latter in aqueous $Na_2S_2O_3$ solutions for 3–5 min is used as in the case of $Ni_2[Fe(CN)_6]$; the process occurring under these conditions is described by the equation

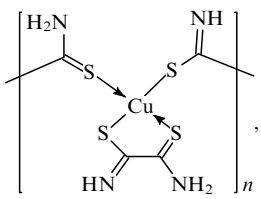
$$Ag_4[Fe(CN)_6] + 8S_2O_3^{2-} \longrightarrow 4[Ag(S_2O_3)_2]^{3-} + [Fe(CN)_6]^{4-}. \quad (12)$$

After bleaching and fixation, copper(II) hexacyanoferrate remains in the photographic emulsion, imparting a red or red-brown colour to the photographic image. The optical densities of this intermediate nonsilver image are fairly high and,when it is observed through a blue light filter, they actually exceed the densities of the initial silver image.[11, 12] There are data showing that the bleaching with the 'copper hexacyanoferrate oxalate' bleaching agent affords higher optical densities of the intermediate metal hexacyanoferrate image than bleaching with the 'copper hexacyanoferrate citrate' bleaching agent.[84] The reason for this difference has not so far been elucidated, but it is undoubtedly not in any way related to the difference between the covering powers of the $Cu_2[Fe(CN)_6]$ constituting this image because subsequently, during toning under identical conditions, the optical densities of the metal chelate nonsilver images obtained are found to be different. Presumably, in the case of the 'copper hexacyanoferrate citrate' bleaching agent the $Cu_2[Fe(CN)_6]$ formed during bleaching dissolves to a slight extent, whereas in the case of the 'copper hexacyanoferrate oxalate' bleaching agent the dissolution does not occur at all or its extent is much smaller because the citrate anion forms more stable coordination compounds with copper(II) than does oxalate.[85]

The formation of nonsilver images from copper(II) coordination compounds of dithiooxamide has been most thoroughly investigated.[44, 53, 60, 61] According to the results of a number of investigations [44, 53, 60, 61]), when the photographic emulsion containing $Cu_2[Fe(CN)_6]$ comes into contact with an alkaline (pH ≃12) solution of dithiooxamide, the water-insoluble coordination polymers



16 (brown-green)

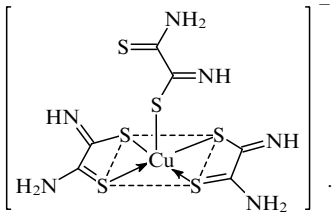


17 (dark-green)

are formed. They are structurally analogous to polymers **4** and **5** and the polymeric copper(II) hydroxide. The last compound arises as a result of the alkaline degradation of $Cu_2[Fe(CN)_6]$:

$$n Cu_2[Fe(CN)_6] + 4n OH^- \longrightarrow 2[Cu(OH)_2]_n + n[Fe(CN)_6]^{4-}. \quad (13)$$

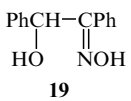
It is noteworthy that copper hydroxide accumulates in appreciable amounts in the gelatin emulsion of the treated photographic material only at extremely low ($< 10^{-5}$ M) concentrations of dithiooxamide in the toning solution in contact with this material.[61] The optical densities D' of the nonsilver images based on the copper(II) complex of dithiooxamide are appreciably higher than the optical densities of the images based on nickel(II) chelates (cf the studies described in Refs 29 and 30, on the one hand, and that in Ref. 53, on the other). However, the image based on copper(II) chelate complexes of dithiooxamide also decomposes readily at fairly high ligand concentrations in the toning solution ($\sim 1.5 \times 10^{-2}$ M), like the image based on nickel(II) chelates, as a consequence of the formation of soluble 1 : 3 complex **18**, to which the following structure has been attributed:



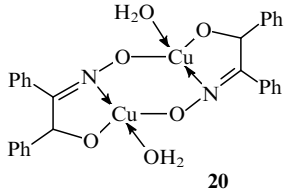
18

This factor should lead to the appearance of maxima on the $D' = f(c_F, c_L^0, t)$ curves.[60,61] The difference between the shapes of the kinetic curves in the nickel(II)–dithiooxamide and copper(II)–dithiooxamide systems consists only in the fact that the degradation of the copper(II) chelate image begins at higher ligand concentrations in the toning solution than the degradation of the nickel(II) chelate complex of dithiooxamide.

Complexes with analogous compositions and structures are formed also in the course of the generation of nonsilver images from copper(II) chelate complexes of quinoxaline-2,3-dithiol.[45,60] According to the present author's data,[60] dimeric copper(II) chelate complexes with the above ligand have the 2 : 2 and 2 : 4 compositions (depending on the degree of deprotonation of the ligand). Nonsilver images based on copper(II) chelate complexes of α-benzoin oxime **19**, distinguished by a very high resolving capacity, not inferior to that of the initial silver image, have also been described in the literature.[46,86] Judging from all the available evidence, in this case the dimeric bright-green chelate **20** is formed in the photographic emulsion.

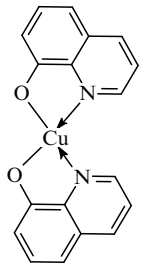


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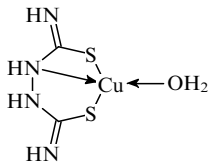


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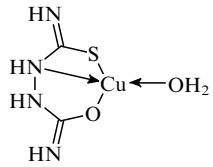
The copper(II) complexes of 8-hydroxyquinoline (the bright-green complex **21**),[48] 8-mercaptoquinoline, bis(thiocarb-amoyl)-hydrazine (the black complex **22**), and 1-carbamoyl-2-thiocarbamoylhydrazine (the black-brown complex **23**) have also been described.[50,60,62]



21



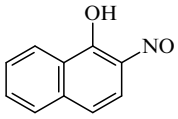
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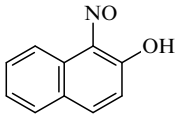
23

In the last two cases, nonsilver photographic images are obtained, the colour and optical characteristics of which are extremely close to those of the initial silver image. Several studies have been devoted to the nonsilver images based on copper(II) chelate complexes of various 3-benzoylthioureas RHN–C(S)–NH–C(O)Ph, where R is an aryl group with bulky substituents.[55–59] In most cases, the photographic images have colours with 'warm' tones, the tints of which are determined both by the nature of the chelating agent and the concentration-time regime in the toning stage.[7,8,60]

Only two cobalt(II) coordination compounds used as carriers of nonsilver photographic images are known at present, namely the chelate complexes of 2-nitroso-1-naphthol **24**[65,71,73] and the isomeric 1-nitroso-2-naphthol **25**.[73]



24



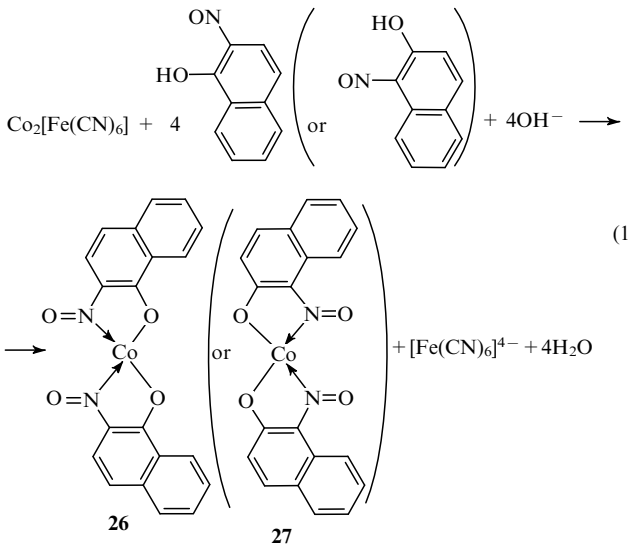
25

According to the literature,[65,71,73] these images are formed in four stages: bleaching [4% aqueous $K_3Fe(CN)_6$ solution, 10–12 min, 20–25 °C]; intermediate toning (5% aqueous $CoCl_2$ solution, 10 min, 20 °C); fixation (25% aqueous $Na_2S_2O_3$ solution, 3–5 min, 20–25 °C); generation of the nonsilver image (1–10 min, 20 °C). The first three stages correspond to the generation of the intermediate image. The process occurring under these conditions are described by Eqns (14)–(17) respectively:

$$4[Fe(CN)_6]^{3-} + 4Ag \longrightarrow Ag_4[Fe(CN)_6] + 3[Fe(CN)_6]^{4-}, \quad (14)$$

$$Ag_4[Fe(CN)_6] + 2CoCl_2 \longrightarrow Co_2[Fe(CN)_6] + 4AgCl, \quad (15)$$

$$AgCl + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^-, \quad (16)$$



(17)

26 **27**

The intermediate image obtained on $Co_2[Fe(CN)_6]$ has a pale-green colour, whereas the images based on the chelates **26** and **27** have dark-red and brick-red colours respectively[65, 71, 73] with extremely high optical densities in green and blue light. With increase in the duration of the fourth stage (toning) and also with increase in the concentrations of both isomeric nitrosonaphthols in the toning solution, the densities D' increase monotonically, tending to certain limiting values.[73]

Despite the fact that cobalt(III) forms a much greater number of coordination compounds with chelating and macrocyclic N,O-, N,S-, and N,O,S-donor ligands compared with cobalt(II), only very few of them have been used as carriers of photographic nonsilver images.[66–70, 72, 74] The synthesis of nonsilver images based on cobalt(III) chelates from initial silver images can be achieved in three stages. The first two correspond to the formation in the photographic emulsion of an intermediate image from cobalt(III) hexacyanoferrate, whilst the third corresponds to the formation of the target metal chelate image. Bleaching is carried out in the course of 20–25 min at 20–25 °C in the 10 g $CoCl_2 \cdot 6H_2O$ + 50 g Na_3HCt (or K_3HCt) + 4 g H_4Ct + 4 g $K_3Fe(CN)_6$ + 0.2 g L-methionine + H_2O (up to 1 litre) solution. Fixation is carried out in 25% $Na_2S_2O_3$ solution at 20–25 °C for 3–5 min. According to literature data,[66, 70, 74] the processes occurring under these conditions can be described by Eqns (18) and (16) respectively:

$$3[Co(HCt)_2]^{3-} + 4[Fe(CN)_6]^{3-} + 4Ag + 3K^+ \longrightarrow \quad (18)$$
$$\longrightarrow 3KCo[Fe(CN)_6] + 4Ag^+ + [Fe(CN)_6]^{4-} + 6HCt^{3-}.$$

The optical densities of the intermediate nonsilver image thus obtained, measured through blue, green, and yellow light filters, greatly exceed the optical densities of the initial silver image.[84] It is interesting to note that the $D' = f(D^{Ag})$ relations for such images on negative phototechnical films have a distinct maximum,[84, 87] whereas on radiographic films there is no such maximum. This difference was attributed [87] to the different degrees of graininess of the photographic emulsions comprising the materials indicated.

The processes leading to the formation of nonsilver images from cobalt(III) chelates have been analysed in greatest detail in a study by the present author,[74] who noted, in particular, extremely complex $D' = f(D^{Ag})$ relations on formation of images with carriers comprising cobalt(III) chelate complexes with ligands such as dithiooxamide, *N*,*N*′-diphenyldithiooxamide, and *N*,*N*′-diphenylthiooxamide. According to the present author,[74] this form of the curves may be fairly adequately interpreted in terms of the concept of stepwise complex formation in accordance with Eqns (19)–(21):

$$4Co[Fe(CN)_6]^{-} + 4 \text{ (RHN, NHR; S, S(O))} + 4OH^- \longrightarrow \quad (19)$$
$$\longrightarrow \left[\text{(RHN, S, Co, S, RN, (O))}\right]_4[Fe(CN)_6]_2 + 2[Fe(CN)_6]^{4-} + 4H_2O,$$

28

$$\mathbf{28} + 4 \text{ (RHN, NHR; S, S(O))} + 4OH^- \longrightarrow \quad (20)$$
$$\longrightarrow \left[\left(\text{RHN, S, S, RN, (O)}\right)_2 Co\right]_4[Fe(CN)_6] + [Fe(CN)_6]^{4-} + 4H_2O,$$

29

$$\mathbf{29} + 4 \text{ (RHN, NHR; S, S(O))} + 4OH^- \longrightarrow \quad (21)$$
$$\longrightarrow 4\left(\text{RHN, S, S, RN, (O)}\right)_3 Co + [Fe(CN)_6]^{4-} + 4H_2O.$$

30

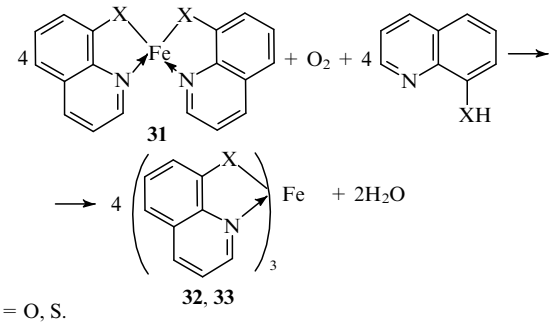
It is noteworthy that, in contrast to the nickel(II) and copper(II) chelates, in the generation of nonsilver images from cobalt(III) chelate complexes of dithiooxamide a dependence of the nature of the $D' = f(\lg H)$ and $D' = f(D^{Ag})$ curves on the type of photographic material in which the initial silver image had been formed is observed. Thus,in the case of radiographic or direct positive films, these curves have a single maximum,[66, 74] whilst in the case of negative phototechnical films there are two maxima,[66, 70] the first of which corresponds to the maximum observed on these photographic materials for intermediate cobalt(III) hexacyanoferrate images, while the second is located in the region of lower values of $D^{Ag}(\lg H)$. It is even more remarkable that the second maximum is observed only in measurements through a blue light filter.[66] Another characteristic feature is that, immediately after the attainment of the second maximum, there is a sharp alteration of the colour of the image from amber-yellow to brick-red, which is linked directly to processes (20) and (21).[66, 70, 74] This type of $D' = f(D^{Ag})$ relations is entirely unique and has no analogueswhatever among other nonsilver photographic image generation processes. It must be specially emphasised that the nonsilver images considered exhibit a very high absorption in the visible part of the spectrum, as a result of which the photographic sensitivity of the treated AgHal material may increase during their formation by a factor of 30–50 and more compared with that for the initial silver image,[72, 74] which is of undoubted practical interest. Nonsilver photographic images based on cobalt(III) chelate complexes of 8-mercaptoquinoline, which, like the images based on cobalt(III) chelate complexes of dithiooxamide and its analogues, have a dark-brown colour, have been described;[69] however, these images have not so far been investigated.

Iron(II) or iron(III) chelate complexes should be of greatest interest as 'working materials' for nonsilver images based on coordination compounds of 3*d* elements because iron and its compounds are cheapest and most readily available. Unfortunately, the majority of iron(II) and iron(III) complexes are relatively unsuitable for the generation of nonsilver photographic images because of their weak absorption in the visible part of the spectrum and appreciable solubility in water. For this reason, the list of iron coordination compounds used as carriers for nonsilver images is extremely limited. Only images based on iron(II) chelate complexes of 8-hydroxyquinoline [76, 79, 81] and isonitrosoacetone [77] [the 'iron(II) ion : singly deprotonated form of ligand' ratio is 1 : 20] and iron(III) chelate complexes of 8-mercaptpquinoline (the above ratio is 1 : 3) [78] have been described in the literature. Such images are obtained in three stages: (1) bleaching in the 5 g NH_4FeCt + 2.0 g H_4Tr (H_4Tr = tartaric acid) + 4.5 g $K_3Fe(CN)_6$ + 2.5 g $CuSO_4 \cdot 5H_2O$ + H_2O (up to 1 litre) solution (see Mikhailov and Budnikov [78]) or the 5 g NH_4FeCt + 1.8 g H_4Tr + 4.0 g $K_3Fe(CN)_6$ + 0.1 g $K_2Cr_2O_7$ + H_2O (up to 1 litre) solution (see Mikhailov and Polovnyak [77]); (2) fixation in 25% aqueous $Na_2S_2O_3$ solutions; (3) transformation of the intermediate image arising in the bleaching stage into the metal chelate image. The intermediate image is coloured sky-blue or blue and has an extremely high optical density in red light.[84] It could have full independent practical importance were it not for its low resistance to photodegradation by UV and visible light and also by alkaline agents. The generation of this image can be described by Eqns (12) and (22):

$$2Fe_2(HCt)(HTr) + 4[Fe(CN)_6]^{3-} + 4Ag + 3K^+ \longrightarrow \quad (22)$$

$\longrightarrow 3KFe[Fe(CN)_6] + [Fe(HTr)_2]^{3-} + 2HCt^{3-} + Ag_4[Fe(CN)_6]$

The most promising ligand for the generation of photographic iron chelate images is 8-hydroxyquinoline, which forms the dark-brown compound **31** with iron(II), It imparts to the gelatin emulsion of the photographic material a colour which is very close to that of the initial silver image but with higher optical densities.[79] In the course of the formation of nonsilver images with such a carrier, compound **32** is formed simultaneously (in a small amount).[76, 79]



(23)

X = O, S.

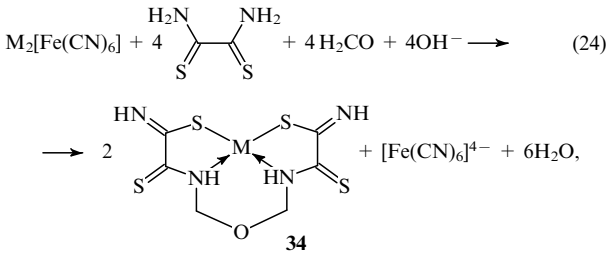
This reaction was not detected in the formation of nonsilver images from iron(II) chelate complexes of isonitrosoacetone (which are coloured blue).[77] However, the oxidation-reduction reaction (23) is decisive in the formation of nonsilver images from the iron chelate complexes of 8-mercaptoquinoline (coloured orange). According to Mikhailov and Budnikov,[78] the emulsions contain exclusively tris(8-mercaptoquinolinato)iron(III) **33**, while bis(8-mercaptoquinolinato)iron(II) was not detected in the photographic emulsion in appreciable amounts of any kind.

Summarising, one should note that the concrete result of the transformation of the silver image into the metal chelate nonsilver image — intensification or attenuation compared with the initial silver image — depends significantly not only on the nature of the chelate complex constituting the image and the concentration — time regime in the toning process but also on the type of photographic material. It has been noted that intensification of the image is usually observed on the photographic emulsions of radiographic AgHal materials, whereas the image is actually attenuated in the photographic emulsions of negative phototechnical and direct positive films.[13–20, 43–51, 65–67] This factor has been attributed to the greater 'covering power' (the ratio of the optical density of the image and the concentration of the carrier present in it) of silver in images on the last two types of photographic materials, as a consequence of which lower concentrations of silver in the initial image correspond to the same optical density in the case of phototechnical and direct positive films compared with the concentration in the case of radiographic films, as a result of which smaller amounts of the hexacyanoferrate(II) of the corresponding metal are deposited together with the silver(I) compounds in the course of bleaching.

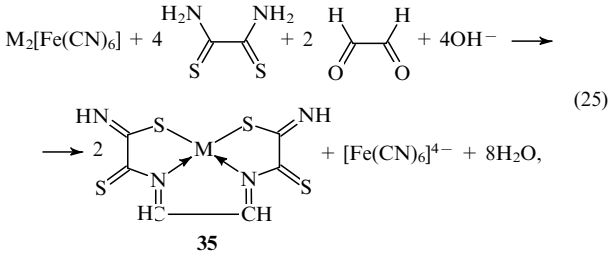
It is noteworthy that in a number of instances the nonsilver images on AgHal photographic materials may be obtained by means of a short procedure: for this purpose, the initially exposed photographic material is developed and is then immediately treated without fixation (the fixation stages have been used in some studies[11–81]) by the procedure described above involving the transformation of the silver image into a metal chelate nonsilver image. Despite the shortening of the overall duration of the treatment, it is then possible to accelerate and render more complete the bleaching of the silver formed in the photographic emulsion after the development stage. However, this possibility has been indicated only in patent publications.[88–92]

Mikhailov and Polovnyak[86] measured certain quantitative structural characteristics of metal chelate nonsilver images and in particular their resolving power. These measurements demonstrated that in most cases the given parameters differ extremely little from the analogous parameters for the initial silver image. This indicates the possibility of employing such images even for defectoscopic purposes, in particular in medical radiography. The data on the resolving power of nonsilver images based on copper(II) chelate complexes of α-benzoin oxime[86] give grounds for the hope that the carriers entering into their composition may be recommended for the generation of images on holographic materials, where the most severe requirements must be met by the resolving capacity of photographic materials.[1] It is striking that the decrease in the resolving power of nonsilver metal chelate images compared with that of the initial silver image has been noted predominantly in those cases where the chelate constituting the image undergoes partial degradation during complex formation as a consequence of its deprotonation or the attachment of additional ligand molecules, which is accompanied by the formation of soluble complexes.[86]

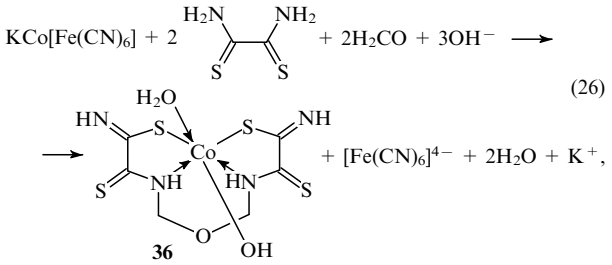
Data have recently appeared in the literature concerning the possibility of obtaining nonsilver photographic images consisting of coordination compounds of *d* elements with macrocyclic ligands during their so called mild template synthesis in metal hexacyanoferrate gelatin-immobilised matrix systems.[41, 42, 63, 64, 93–95] The carriers for such nonsilver images are cobalt(III), nickel(II), and copper(II) coordination compounds of 2,8-dithiono-3,7-diaza-5-oxanonane-1,9-dithioamide and 2,7-dithiono-3,6-diazaocta-3,5-diene-1,8-dithioamide (complexes **34**–**37**), arising when photographic emulsions containing cobalt, nickel, and copper hexacyanoferrates come into contact with dithiooxamide–formaldehyde or dithiooxamide–glyoxal toning solutions. According to the literature,[41, 42, 63, 64, 93–95] the following reactions occur in this case:



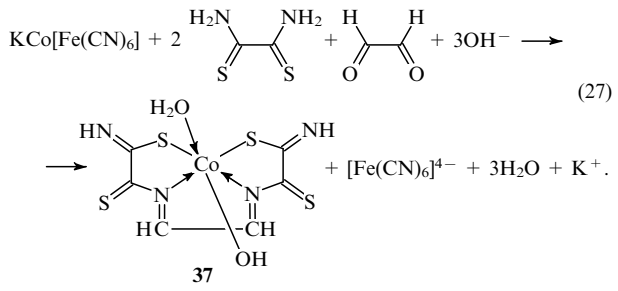
(24)



(25)



(26)



(27)

37

The generation on AgHal photographic materials of nonsilver images with carriers of this kind makes it possible to achieve an appreciable increase in photographic sensitivity (almost by two orders of magnitude) compared with that for the initial silver image.[64, 93–95] Judging from the literature data,[41, 42, 63, 64, 93–95] the use of template synthesis reactions gives rise to new possibilities for the synthesis of metal chelate nonsilver images and large scale studies are clearly necessary in this field.

There are indications of the possibility of obtaining polychromic metal chelate nonsilver images in which the nickel(II) coordination compounds of *N*,*N*′-diphenylthiooxamide, dimethylglyoxime, and dithiooxamide, already mentioned, serve as the yellow, purple, and sky-blue components, although unfortunately this possibility has not so far been realised in practice.[96]

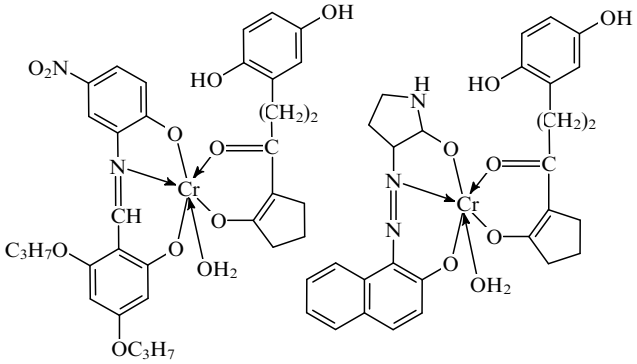
III. Metal chelates and metallomacrocycles in the colour photographic process with diffusional transfer of the image

In the photographic processes examined in Section II, the nonsilver photographic images with metal chelate carriers arose in the photographic emulsion of the initial AgHal photographic material as a result of the transformation of the silver image produced on it initially into the non˜silver target image via a series of specific chemical reactions. The individual stages of the process leading to the transformation of the silver image into the nonsilver one were then separated both in space and in time. However, it is possible to imagine a AgHal photographic system in which these metal chelates or their derivatives are already present initially in a 'pure form' whereupon the nonsilver image is formed in one stage. This version of the single-step AgHal process, in which exposure and the chemical-photographic treatment take place simultaneously, was proposed in 1947 by the American inventor E Land.[97] In the process which he proposed, the light-sensitive emulsion of the exposed photographic material immediately came into contact with photographic paper containing a special layer of varnish. In the course of the chemical-photographic treatment, particles of the metal chelate dye, creating a negative image in the photographic material, remained on the exposed sections, whereas the particles of the dye remaining on the unexposed sites of the photographic material diffused into the receiving layer of the photographic material on an opaque support (usually photographic paper), where the positive coloured image was in fact created.

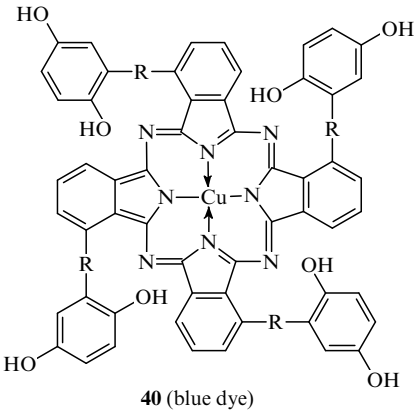
In the photographic process with diffusional transfer of the image, photographic materials consisting of three layers are usually employed.

Each of them is in its turn divided into two sublayers: the upper light-sensitive layer containing AgHal and reacting selectively to red, green, or blue light and the lower layer with an intensely coloured metal chelate, the colour of which is 'complementary' to that of the zonal sensitivity of the upper sublayer (namely sky-blue, purple, and yellow). The nonsilver image consists of a mixture of the above dyes, the ratio of which in the ultimate image depends primarily on the level of exposure and the spectral composition of the exposing radiation,so that the image is almost always polychromic. The carriers of these images are usually none other than intensely coloured coordination compounds of 3*d* elements with N-, N,O-, or N,S-containing chelating or macrocyclic ligands.[98–137] This type of AgHal photographic process has been called a colour diffusion photographic process; several reviews have been devoted to it.[106, 110, 138–140]

At the present time the most popular is the AgHal photographic process where the purple and yellow colouring components are chromium(III) coordination compounds of azomethine dyes or azo-dyes, while the sky-blue component is a copper(II) chelate complex of the macrocyclic phthalocyanine formed in the course of template synthesis.[98–109] Thus the chelates **38**–**40** have been used.[101] The SX-70 Polaroid photographic material with diffusional transfer of the photographic image (USA) is widely known. Dyes of the above or similar composition are used in it as the colour components.[105] Judging from all the available evidence, the combination of the chelate complexes **38**–**40** is altogether one of the most successful.



38 (yellow dye) **39** (purple dye)

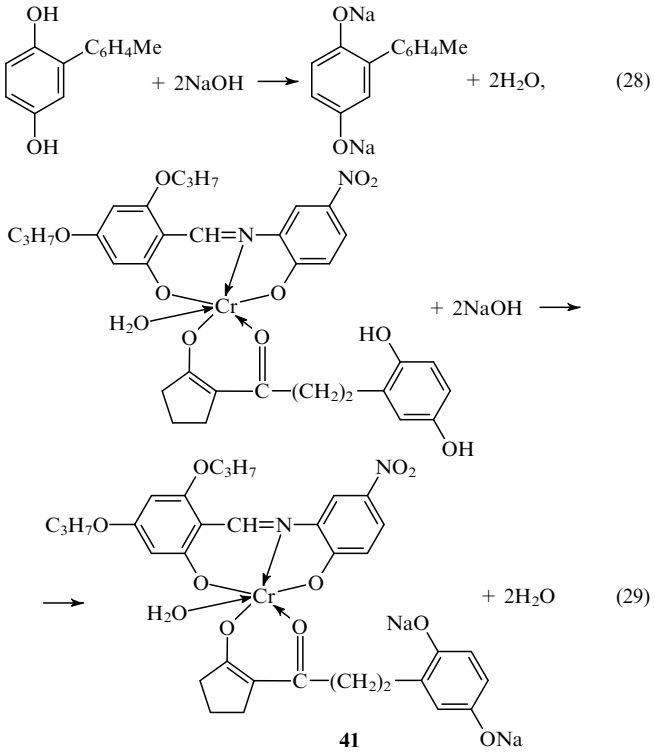


40 (blue dye)

R = –SO$_2$NHCH(Me)CH$_2$–

Other chromium(III) coordination compounds have also been proposed as reagents for the generation of nonsilver metal chelate images, but, so far as we are aware, they have not found any kind of appreciable practical use.

The nonsilver image formation processes in the colour diffusion photographic process have been described in detail.[106, 110] For chemical photographic treatment of photographic materials with diffusional transfer of the photographic image, use is made of compositions an obligatory element and active principle of which is NaOH, KOH, or another alkaline agent. Diffusing in the course of the photographic treatment in the light-sensitive layer, the alkaline agent ionises the developing substance present in the photographic emulsion (this is usually methylphenylhydroquinone, which performs the same function in this instance as in the standard AgHal photographic process) and the colouring components. An example of the ionisation of a yellow dye is presented below:

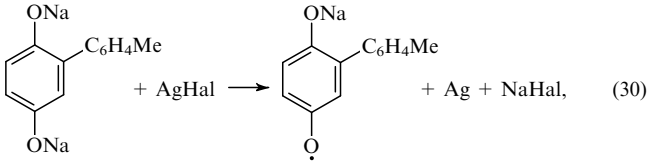


(28)

(29)

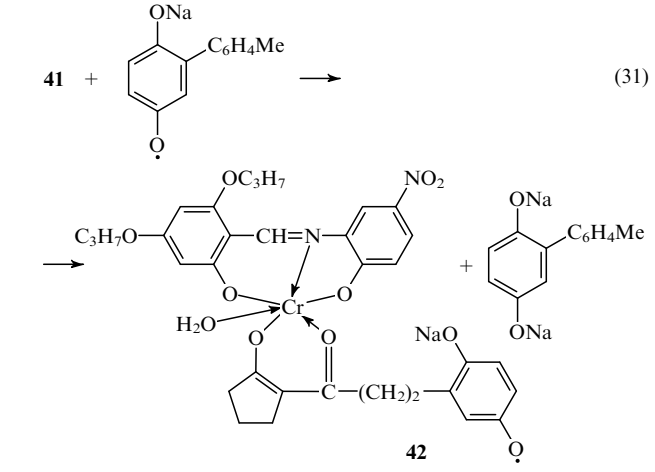
41

On the exposed regions, sodium (or potassium) methylphenylhydroquinonate reduces AgHal [Eqn (30)],being converted at the same time into the corresponding radical-ion:



(30)

By subtracting an electron from the ionised form of the dye, the radical-ion transforms it into the semiquinone form. A scheme illustrating the formation of semiquinones for a yellow dye is presented below:



(31)

42

The semiquinones are fairly readily converted into insoluble dyes, incapable of diffusion and not coming into contact with the reception layer. On the unexposed sections of the photographic material, where the semiquinones are not formed, the soluble forms of the colouring components (the ionised forms) permeate into the reception layer and come into contact with the photographic paper, being at the same time reconverted into the insoluble forms. A nonsilver metal chelate image is formed on the photographic paper as a result.

Apart from the coordination compounds **38**–**40**, there is of course a possibility of using also other representatives of complexes of the given class. Thus it has been suggested that cobalt(II) and nickel(II) complexes of phthalocyanines [119] and the chelate β-ketoacetamidoimidazoquinoline complexes of a series of *d* elements,[120] which exhibit a very high resistance to the action of radiation and corrosive agents in the environment, be employed. In a series of studies carried out in recent years, the possibility of using the coordination compounds of nickel(II),[121–125, 131, 133, 135] cobalt(III),[128] and also platinum group metal ions, in particular those of rhodium(III) [129] and palladium(II),[123, 125, 131, 137] in the colour diffusion photographic process has ben considered. Judging from all the available evidence, a very large number of coordination compounds with structurally cumbersome N,N′-N,O-, and N,S-chelating and especially macrocyclic ligands having high extinction coefficients in the visible part of the spectrum are suitable for effecting the colour photographic process with diffusional transfer of the image.[129, 131] The use of compounds **38**–**40** is associated primarily with their availability and low cost.[110, 138, 139]

IV. Chelate and macrocyclic complexes as the 'active principle' of nonsilver photographic systems

Several decades before the silver halide photographic process saw the light of day, namely in 1831, Döbereiner already observed that potassium tris(oxalato) ferrate(III) $K_3[Fe(C_2O_4)_3]$ exhibits an extremely high sensitivity to ultraviolet and blue radiation. Döbereiner's observation for a long time failed to attract the attention of investigators even despite the fact that in 1842 J Herschel created on its basis a fundamentally new, for the time, method of recording information — the so called cyanotype method. Its essential feature reduced to the fact that the photolytic redox process

$$2[Fe(C_2O_4)_3]^{3-} \xrightarrow{h\nu} 2[Fe(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2. \qquad (32)$$

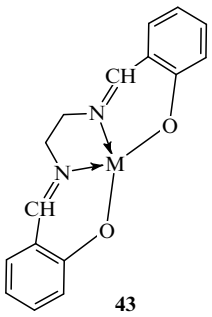
occurred on the sections of the paper impregnated with $K_3[Fe(C_2O_4)_3]$ solution subjected to illumination by quanta in the ultraviolet and visible (blue zone) regions of electromagnetic radiation.

The 'working material' for the generation of the visible image was in this case the hexacyanoferrate $KFe[Fe(CN)_6]$, which was formed on the exposed sections of the photomaterial, treated with an aqueous solution of potassium hexacyanoferrate, in accordance with the following reaction:

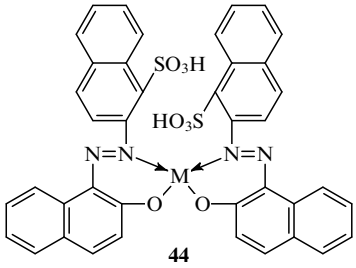
$$[Fe(C_2O_4)_2]^{2-} + [Fe(CN)_6]^{3-} + K^+ \; KFe[Fe(CN)_6] + 2C_2O_4^{2-}. \qquad (33)$$

The unexposed sites remained unchanged after treatment of the exposed photomaterial with $K_3[Fe(CN)_6]$ solution. This resulted in the formation of a blue image on a white background. This process was used in practice (mainly for copying work) up to the 1960s; nowadays it has been displaced by improved methods (in the first place xerox copying) and it is therefore of only historical interest. However, the problem of the search for systems which are not inferior to silver halides as regards their sensitivity to visible radiation remains of current interest.[1] In this connection, the attention of investigators has been attracted by the coordination compounds of *d* elements with chelating and macrocyclic ligands; one cannot rule out the possibility that in the future photographic materials based on them will prove capable of offering serious competition to AgHal light-sensitive systems.[141–145]

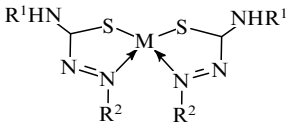
Coordination compounds with N,O- and N,S-ligands, in particular with the azomethines **43** and azo-dyes **44**,[146–150] 8-hydroxyquinoline, anthra-quinone and its derivatives,[151] various substituted derivatives of dithizone and dithiocarbamic acid (compounds **45** and **46**),[152–154] and the structurally similar compound **47** [155] have been proposed as reagents suitable for recording UV and visible radiation.



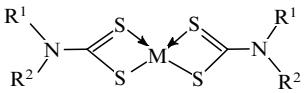
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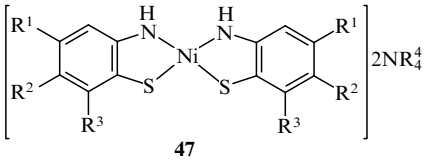


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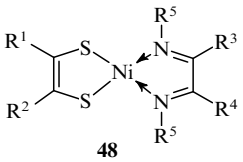
M = ion of 3*d* element; R^1, R^2 = Alk, Ar;



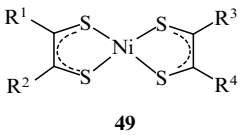
47

R^1, R^2, R^3 = H, Alk, NO_2, Hal, NR'_2.

Also proposed have been a series of coordination compounds with dithiolate ligands (in particular complexes **48**–**50**),[156–161] *i.e.*

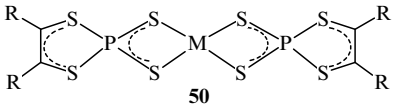


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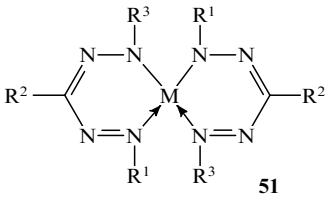
R^1–R^5 = Alk, Ar;



50

M = V, Ni, Cu, Pt; R = Ph, Ar, AlkO

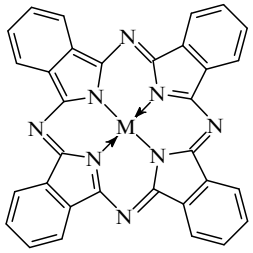
and with N,N-donor ligands,[162–189] among which special mention should be made of the zinc(II), cobalt(II), and mercury(II) coordination compounds of benzindolinospiropyrans,[162] the copper(II) complexes of 1,2-ethylenediamine and its analogues $[CuL_n](BR_4)_2$ (n = 2–4, R = Ar),[163,164] and compound **51**.[169]



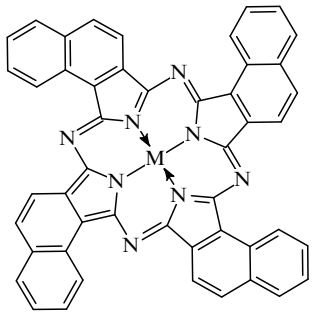
51

M = Mn, Co, Ni, Cu, Pd, Pt;
R^1–R^3 = H, Hal, OH, COOH, Alk, AlkO, Ar.

However, coordination compounds with various phthalocyanine ligands, the simplest of which is complex **52**, aroused the greatest interest. Initially complexes of this type were used as carriers of the nonsilver photographic image;[170] however, the role of the light-sensitive compounds was assumed by coordination compounds of the type $[PdL_mX_n]_kY_l$ [L = sterically hindered polydentate ligand of the type of 1,1,7,7-tetraethyldiethylenetriamine; X = Cl, Br, N_3, SCN; Y = Cl, Br, N_3, SCN, $B(OR)_4$; m, n = 1,2; k, l = 1–4] while the leuco-forms of the phthalocyanine complexes served as a kind of 'developing substances'. However, studies have been published recently[171–186] where macrocyclic coordination compounds of this kind were used this time as radiation receptors. Thus Mn(III) and V(IV)O alkylphthalocyanines have been proposed for the recording of information with the aid of a semiconductor laser,[171] 1,2-benzophthalocyanines **53** have been proposed as optical recording materials,[172,176] and fluoroalkylated phthalocyanines have been suggested for the recording of laser radiation.[177]

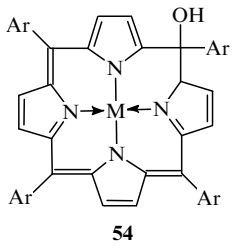


52 (M = Ni, Cu)



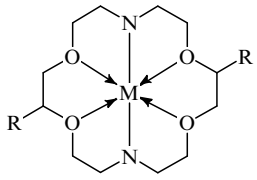
53

The use of coordination compounds of 3*d* elements with related phthalocyanine ligands, in particular the cobalt(II), nickel(II), and copper(II) complexes of substituted tetrapyrazinoporphyrins[187,188] and the gold(II) and palladium(II) complexes of hydroxyphlorins (complexes **54**[189]) as light-sensitive reagents has also been described.



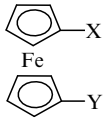
54

Quite a few instances of the successful employment of coordination compounds of metals with hydroxyacids (the photochromic properties of such compounds have been known for a long time) as well as other O,O-ligands (in particular β-diketones and crown-ethers[190–200]) are known.



M = Co, Ni, Cu.

There are also literature data concerning the fairly high sensitivity of carbonyl and cyanide complexes to UV and visible light quanta,[200–205] in particular their practical application as the active principle in a series of photochromic systems.[206,207] The use of ferrocene and its derivatives,[208–215] for example the products of its interaction with the salts of quaternary heterocyclic bases,[208] for this purpose is extremely instructive Thus photographic emulsions recording radiation as far as the blue-green region of the visible spectrum have been prepared on the basis of complex **55**.

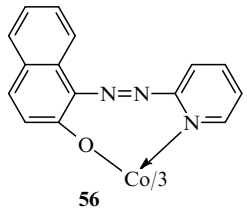


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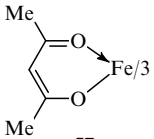
X, Y = $CO(CH{=}CH)_nAr$ (n = 1, 2)

In certain nonsilver systems based on the titanium(IV) chelate complex of 8-hydroxyquinoline,[152] it was possible to achieve a comparatively high sensitivity of the photographic emulsions to light quanta over the entire visible range (400 – 700 nm), but the level of sensitivity of the AgHal photographic materials in the same range has not so far been attained. In most cases, the coordination compounds with chelate and macrocyclic ligands are sensitive only to radiation in the UV and blue-violet (< 430 nm) spectral regions furthermore, the lower limit of the level of radiation per unit surface of the photographic emulsion which they are still capable of detecting (it can be regarded as a kind of characteristic equivalent to photographic sensitivity) is $\sim 10^{-3}$ J cm^2, whereas for modern silver halide photographic systems it is close to 10^{-7} J cm^2.[214] Data concerning the possibility of using the coordination compounds of metals with chelate and macrocyclic ligands for the recording of streams of fast electrons, X-rays, γ-rays, and other types of high-energy radiation are more promising in this connection.[216 – 229] In particular, the ferrocenyl complexes **55** as well as the analogous nickel(II) cobalt(II), chromium(III), and titanium(IV) complexes, already mentioned above, have been used for this purpose, as a result of which it proved possible to record electron streams and X-rays with energies up to 20 keV.

Even more interesting data have been obtained on cobalt(II) chelate complexes with 1-(2-pyridazo)-2-naphthol ligands (complex **56**), *i.e.*



56



57

which in terms of sensitivity to ionising radiation in general and to X-rays in particular are superior to silver halides. The copper analogue of complex **56** with a metal ion : ligand ratio of 1 : 2 also exhibits a fairly high sensitivity to electron streams.[223] The coordination compounds of cobalt(III) with other tridentate ligands, in particular with 1-(2-pyridyl-, 1-(2-thiazolyl)-, and 1-(2-oxazolyl)-formazans, and also with 1-(2-pyridyl)-1-(2-quinolinyl)-dithiooxamide may also serve as the active principle in light-sensitive systems.[220] A comparatively high sensitivity to X-rays has been noted also in the iron(III) chelate complex of acetylacetone **57**.[219]

The same complex can be used for the reception and brief fixation of information under the influence of high-intensity radiation, in particular laser radiation. There is no doubt that the list of coordination compounds of *d* elements with chelating and macrocyclic ligands may increase appreciably in the future. Bearing in mind that silver halide photographic materials with extremely high AgHal concentrations per unit surface are used for the recording of hard ionising radiation in medical and especially industrial radiography,[230] the interest of investigators in these materials becomes understandable.

Unfortunately at the present time there have been few detailed studies of the mechanisms of the formation of nonsilver images in light-sensitive systems comprising coordination compounds with chelating and macrocyclic ligands.[175, 195, 231 – 233] The mechanism of the formation of images in photographic emulsions containing organopolysilanes and titanyl(IV) phthalocyanine as a result of their exposure to UV radiation has been examined.[175] The photocolouring process and the photodecolorisation of titanium(IV) coordination compounds of hydroxy-acids under the influence of UV and visible radiation has been investigated; the authors [175] believe that the photochromism observed in this case is associated with the redox process

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

This hypothesis is supported if only by the fact that the colour of the photochromic solution vanishes not only in the dark but also on oxidation, for example by atmospheric oxygen.[175]

A short but extremely interesting paper [232] in which the mechanism of the absorption of radiation by the chromium(III), iron(III), cobalt(II), nickel(II), and copper(II) coordination compounds of azo-dyes, in particular 2-hydroxyphenylazo-2-naphthol and 2-carboxy-4-methylphenylazo-4,5-diphenyltriazo also merits attention. A relation has been established between the ability of these compounds to record radiation and the formation in their presence of singlet oxygen. The image formation process in photographic emulsions based on ferrocene has been examined [212, 215] and the effect involving the reversal of the image under the influence of a small amount of reagents capable of forming stable coordination compounds with iron(II) and iron(III) was noted. In this connection, the hypothesis was put forward [212] that such reagents bind iron(II) and (or) iron(III) and eliminate them from the autocatalytic process involving the reduction of ferrocene and actually play the role of a kind of inhibitors (the virtually complete inhibition of the development process is observed even at extremely low concentrations of these substances, namely ~0.003 M).

An attempt has been made to interpret the light-sensitive properties of tris(2,2-bipyridyl)ruthenium in photoinduced film stencils made from organic pigments,[233] whilst in another study [231] photographic systems with an 'active principle' comprising copper(I) and cobalt(III) coordination compounds were considered; mechanisms of the formation images on the corresponding photographic materials have been proposed in individual instances.

Overall, it is essential to note that, despite the existence of a fairly considerable set of review articles and monographs (see, for example, Refs 138 – 145, 234, and 235), the studies on the mechanisms of the formation of photographic images on nonsilver light-sensitive materials are narrowly specific and scattered. Furthermore, the sensitisation possibilities remain completely undiscovered for nonsilver photographic systems based on coordination compounds of *d* elements with chelating and macrocyclic ligands (as is the case for AgHal photographic materials), so that the true potential possibilities of such light-sensitive systems remain in essence completely unknown. The sensitometric characteristics of the nonsilver photographic materials which might be realised in practice by varying the processes involved in their chemical-photographic treatment also still remain obscure. The mechanisms of the formation of catalytic centres in nonsilver light-sensitive systems based on coordination compounds with chelating and macrocyclic ligands have also been inadequately investigated. (In the vicinity of these centres, the development reaction, accompanied by the formation of a carrier of the nonsilver image in the photographic emulsion, is known to occur first of all.[2, 3]) The coordination of the efforts of specialists in two extremely remote fields of science — the photochemistry of the information recording processes and coordination chemistry — is essential for the successful solution of the problem. Unfortunately one has to conclude that in recent years interest in the search for and study of nonsilver photographic systems based on chelate and macrocyclic coordination compounds has appreciably diminished despite the fact that there has been no real increment in the extraction of silver throughout the world and, judging from all the available evidence, cannot be expected in the foreseeable future.

V. Conclusion

The nonsilver photographic systems and photographic images examined in this review, the carriers of which are coordination compounds of *d* elements with chelating and macrocyclic ligands, are of considerable interest both for photographic science and for the chemistry of coordination compounds. The generation of metal chelate photographic images can increase in many instances the information content in light-sensitive materials. Furthermore,

one may expect in the future also the creation of a colour photographic process analogous to current silver halide colour photography, in which the image carriers will be coordination compounds of *d* elements with chelating and macrocyclic ligands. They will ensure the highest resistance of photographic materials to the action of light and corrosive agents in the environment. There are all possible grounds for the assumption that, as new experimental data accumulate, this global problem in modern photography will be successfully solved.

As regards the chemistry of coordination compounds, the synthesis of complexes of 3*d* elements with chelating and macrocyclic ligands marks the appearance of an independent scientific disipline — the study of the reactivities of polymer-immobilised coordination compounds with fixation of the substance by intermolecular forces and the discovery of the rules governing complex formation involving such compounds.[9]

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