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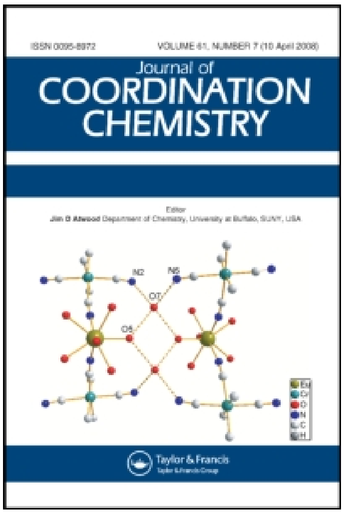

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COORDINATION COMPOUNDS IN SILVER HALIDE PHOTOGRAPHY

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The data on the main aspects of usage of coordination compounds with nitrogen-, oxygen-, and sulphur-containing ligand in various spheres of a silver halide photographic process at different stages of precipitation of light sensitive materials and in their photochemical treatment and additional transformation of the silver image as well as in diffusion transfer systems are summarized. The review covers the period of 1968–1990 with 275 references.

Keywords: Coordination compounds, photographic process, silver halide

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1. INTRODUCTION

During the last 15–20 years, a distinct tendency towards complex usage of coordination compounds in various photographic processes, and first of all, in the most important one, *i.e.*, in silver halide photography, can be noticed. Coordination compounds of metals with organic ligands can be considered as a sort of a "boundary zone" between inorganic and organic chemistry. From this point of view, one may expect a demonstration of useful properties of both organic and inorganic substances which can be utilized in photographic processes.

In general, the photochemical transformation in light-sensitive systems can be expressed by the following scheme:

$$A \xrightarrow{h\nu} B; \quad B + C \longrightarrow D; \quad M^{z+} + \text{Red} \xrightarrow{D,M} M + \text{Ox}$$

where A is a light-sensitive compound, B is a photolysis product of A, C is a compound forming upon the reaction with B the particles of a catalyst D which plays the role of formation centres of a future image, Red is a reducing agent, Ox is a product of its oxidation, M^{z+} is a metal ion, and M is a metal reduced.[1] The functions of all three stages can be performed by at least from one to three compounds. The quantum-mechanical model of a silver halide photographic process has been presented.[2,3] During the irradiation (exposure) of silver halide microcrystals, the extremely fine dispersed silver particles are formed at the sites where irradiation has worked. This process takes place according to the following scheme: a) electron transfer from silver halide valence band to the conduction band, b) electron transfer from the conduction band to the lowest levels due to the presence of impurities in silver halide which act as electron traps, c) diffusion of silver ions into the traps and neutralization of the former with the formation of a photolytical silver

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atom, d) electron capture by a photolytic silver atom with the further attachment of a second silver ion and the formation of a two-atom particle, etc. Halide atoms formed upon the photolysis are absorbed by the system binding component gelatin.[2,3] Thus, the irradiated areas differ from non-irradiated ones. The treatment by special compositions (developers) provides for a faster silver halide rehalogenation in the vicinity of silver particles formed upon the exposure in comparison with the silver halide reduction in the "dark" area; the causes of this phenomenon have been explained.[2-4]

The silver halide photographic process can be divided into three principal stages: the synthesis of a silver halide photographic system, its exposure, and subsequent chemical-photographic processing. The manufacturing technique of these systems is very specific including the following: emulsification (the formation of a dispersion in an aqueous gelatin phase of silver halide microcrystals produced as a result of the exchange reaction of alkali metal halides and silver nitrate), physical ripening (the formation of silver halide microcrystals of a predetermined size and crystal habit), washing (removing the excess of soluble salts with subsequent dispersing in an aqueous gelatin phase free of these salts), chemical ripening (the thermal treatment in the presence of certain compounds providing for the desirable level of a photographic sensitivity), coating the resulting gelatin silver halide suspension of a desirable thickness (called in practice by the incorrect, though conventional, term "photographic emulsion") on a transparent or opaque support. Changing the synthesis conditions and initial material parameters, one can obtain a wide variety of emulsions and photographic materials.[2-4]

Coordination compounds in silver halide photography can be used at different stages of emulsion synthesis, both during chemical processing and silver image transformation, as well as in diffusion transfer processes. These subjects are discussed in this review.

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2. COMPLEX COMPOUNDS AS ADDITIVES AT VARIOUS STAGES OF PREPARATION OF SILVER HALIDE PHOTOGRAPHIC SYSTEMS

The introduction of various compounds into the photographic emulsion usually pursues one of the following aims:[2,3] 1) selective or general increase of the photographic sensitivity to radiation using sensitizers; 2) improved ageing stability of photographic materials or images using stabilizers; 3) partial or total elimination of fog using antifogging agents; 4) improved thermal stability and strength for photographic layers using hardeners; and 5) growth control of silver halide microcrystals during physical ripening using catalysts or inhibitors of crystal growth.

2.1. Coordination Compounds as Sensitizers

The first data on the use of complexes as sensitizers date back to 1939 when the so-called "gold sensitization" was patented.[5] The sharp increase in the photographic sensitivity of a silver halide emulsion was reported when tetrachloroauric(III) acid $H[AuCl_4]$ was introduced into the silver halide emulsion. Later similar properties were demonsrated for other gold complexes. It is characteristic that gold(I) complexes are generally more effective sensitizers than those of gold(III).[6-9] This phenomenon is now associated with partial substitution of silver centres by gold centres which

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behave as better electron traps. Gold(I) sensitizers produce three times more centres in comparison with gold(III) ones.[10] The effect of the substitution is confirmed by the fact that $[Au(CN)_2]^-$ in which the substitution of gold(I) by silver(I) is less likely than in $[Au(SCN)_2]^-$ demonstrates the sensitizing effect less than that observed for $[Au(SCN)_2]^-$. Bisthiocyanatoaurate(I) $[Au(SCN)_2]^-$ is the most effective gold sensitizer providing for the increase of emulsion sensitivity by more than an order of magnitude. The sensitizing effect of noble metal halide complexes has been studied.[11-20] In most cases increase of the sensitivity has been reported in comparison with non-sensitized emulsions. However, results better than those for gold(I) sensitizers can be achieved only for platinum(II) complexes,[3,13] the fog level being noticeably higher. Most authors attributed the mechanism of sensitizing to the partial substitution of silver centres by the centres of other metals nobler than silver in the electrochemical series. Having higher ionization potentials, they are better photoelectron traps than silver particles.[2,3,10] It is reported that the sensitizing effect of chloro-complexes of 4d- and 5d-elements increases with the increase in ionization potential and with the decrease of the ionic charge of the central metal.[3] The sensitizing effect of rhodium(III), iridium(III) and (IV), osmium(III) and (IV), and ruthenium(III) and (IV) complexes with various ligands such as 3,3-dimethylindolenine with oxazole, benzoxazole, or naphthoxazole residues is reported in respect to direct positive emulsions which are in general rather difficult to sensitize.[20] It is interesting to note that the use of noble metal ion complexes other than gold(I) and gold(III) as sensitizers is accompanied by gamma decrease of silver halide emulsions and materials, while in the case of rhodium(III) complexes, this parameter is found to increase.[3,10,17,18]

There are different interpretations of this phenomenon called "rhodium effect" in literature. Tani and Saito[15] associate $[RhCl_6]^{3-}$ sensitization only with substitution of silver centres by rhodium ones. Beck *et al.*[17] suggest that the "rhodium effect" is the result of partial or complete substitution of water molecules in rhodium(III) surrounding for chloride ions. The latter supposition is in agreement with the data presented by others,[21,43] according to which the "rhodium effect" diminishes in the $[RhCl_6]^{3-}-[RhCl_3(H_2O)_3]-[RhCl(H_2O)_5]^{2+}$ series, and completely disappears in $[Rh(H_2O)_6]^{3+}$. The most interesting question, however, is why $[RhCl_6]^{3-}$ has such an effect which is quite different from other noble metal halide complexes, has not yet been discussed. It seems that the keen interest for the search for new sensitizers among noble metal coordination compounds is not reduced but proved by the works in the last five years.[36-43] The search of compounds for "gold sensitization" is still in progress.[40-42] As has been shown recently,[42] along with gold(I) and gold(III) complexes, gold(II) complexes of the type AuLL′, where L is dichalogencarbamete and L′ is maleonitriledithiolate, such as (*N*,*N*′-diethyldithiocarbamato)(maleonitriledithiolato)gold(II), also display a sensitizing effect.

The data on the sensitizing effect of other 3d- and 4d-element complexes are fragmentary and incomplete. Cobalt(III) complexes have attracted a steady attention.[22-30,44,45] Tris-chelated Co(III) complexes of 1,2-diaminoethane (ethylenediamine = en), 1,2-diaminopropane (propylenediamine), di(2-hydroxyethyl)amine (diethanolamine), and their derivatives increase the sensitivity by 2–4 times that of non-sensitized materials but decrease simultaneously the fog level of negative films.

Increase in the optical density of a colour image is observed upon introducing cobalt(III) complexes of uni- and bidentate nitrogen-base ligands such as NH_3, en, into colour photographic materials.[23,24] In the latest work[25] ethylenediaminetetraacetatocobalt(III) complex has been tested. The causes of the sensitizing effect of these

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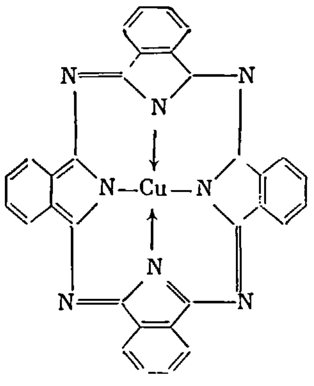
cobalt(III) complexes have not been established in the papers cited. In our opinion, there is a relation with the so-called catalytic dye formation process.[29,30] There are certain data on the possibility of employment of cobalt(III) complexes of uni- and bidentate ligands in order to increase optical densities of direct positive photographic materials.[26] Although no direct evidence is given,[19] it is likely that the effective sensitizing agents are cobalt(III) complexes of zero-methylmerocyanine (rhodamine, thiohydantoin, and thioxazolidinedion derivatives). The data in a patent[28] are of undoubtful practical interest: the template copper(II) complex with phthalocyanine I increases the sensitivity of photographic material to ionizing radiation by 1.5–2.5 times upon the introduction into the emulsion during chemical ripening. When copper(II) complexes of crown-ethers II and III are introduced into superfine-grained silver bromide emulsions, it results in the increase of both the sensitivity and resolution power of a photographic material as well as latent image stability.[31]



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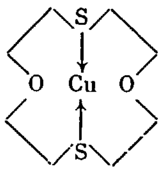

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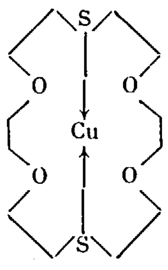
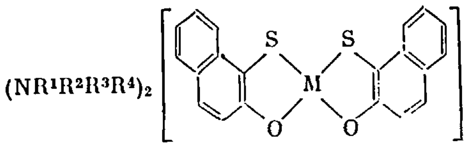
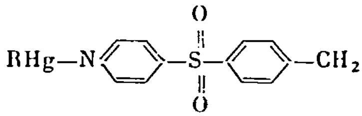


III

Nickel(II) and other group VIII metal complexes are used as sensitizers for various silver halide systems.[19,26,32] Of particular interest among them are the compounds of the general formula IV (R^1–R^4 are aryl, alkyl, or oxyalkyl; M is nickel, cobalt, or platinum) which have been patented as silver halide sensitizers to the infrared region.[32] Good efficiencies are given for the mercury(II) complexes, V, ligated with *N*-phenyl-*n*-toluenesulphamides where R is alkyl, C_1–C_3 are phenyl, tolyl, or benzoyl,[33] and for bis(dipropanolamine)chromium(III) sulphate.[27]



IV



V

In the latter case the effect of the complex is assumed to oxidize hydroquinone in the course of development, although it is doubtful because of the very weak ability of chromium(III) to be reduced in an alkaline medium.

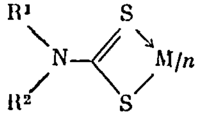
It is of interest that in some cases silver(I) complexes can also act as sensitizers, in particular those with crown-ethers[33] as well as those with thio- and selenoethers in the presence of cyanine dyes.[34] In these cases sensitized emulsions show wonderful stability; no comments have been made on the observed phenomena.[31,34] It is quite possible that in the second case, along with silver centres, both Ag_2S and Ag_2Se centres are formed as better electron traps with a higher stability.[2,3] Charkondian[35] supposed that the sensitizing effect of the silver complexes with nitrogen-containing ligands of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclo-decane type is interpreted in terms of silver(I) disproportionation in the vicinity of latent image centres according to the scheme:

$$2Ag^+ + L \longrightarrow AgL^{2+} + Ag \text{ (L is a ligand).}$$

It can be assumed that similar process is realized during sensitization by the crown-ether silver complexes described in a US patent.[33] No data are available on the sensitizing effect of other coordination compounds, nor can any reviews be found on the subject.

2.2. Coordination Compounds as Stabilizing Agents

The constant attention has been paid to the potential abilities of complexes stabilizing silver halide systems and images formed thereon. The greater part of the works deals with platinum complexes[3] which are used as stabilizers for photographic materials stored under high temperature and humidity conditions. In the first place, it concerns the $K_m[MX_n]$ type compounds where M is ruthenium, rhodium, palladium, iridium, or platinum, K is a univalent cation, $n = 4$ or 6, $m = 2, 3, 4$, and X is a halo ligand.[3] The most active is probably $(NH_4)_2[PdCl_4]$.[3] However, the stabilizing properties of complexes with various nitrogen- and oxygen-containing ligands have been proved only for rhodium(III). The tests have been performed with the rhodium complexes of adenine, guanine, uracil, thymine, and cytosine,[46] and 4-oxo-5-octyl-6-methyl-1,3,3a,7-tetraazaindene and 7-oxy-1,2,3,4,6-pentaazaindene[47] introduced during physical ripening. Several mercury(II) complexes with various aminothiazoles and the above-mentioned compounds V[33] having the same properties, are known as stabilizers. In the latter case, these compounds can prevent the formation of the so-called dichroic (green-yellow) fog in the superfine-grained photographic materials. There is also evidence on the stabilizing effect of cadmium(II), silver(I), and zinc(II) complexes with dithiocarbamates VI, where R^1 is an aryl, alkyl, or heterocyclic group, R^2 is H or R^1, M is a metal, and n is the valence.[48]



VI

The copper(II) chelates of *cis*- and *trans*-isomeric 2-chlorobenzo-hydrazide are employed as stabilizers.[49] It is noteworthy that both isomeric forms have a substantially equal photographic activity. In order to reduce the side effect of a number of organic compounds introduced into photographic emulsions, the empolyment of a heteroligand vanadium(IV) oxalato-peroxide complex $Na_3[VO(O_2)(C_2O_4)_2]{\cdot}6H_2O$ has been proposed.[50] Bismuth(III) intracomplex compounds with nitrogen- and

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oxygen-containing ligands have recently been described as stabilizers for photographic layers to prevent the formation of the yellow fog during storage,[51] as well as palladium(II) and platinum(II) chelates of $[ML_n][BAr_4]_2$ type where Ar is aryl, L is a multidentate ligand with nitrogen and oxygen donor atoms such as those including neutral Levy base.[52] To all appearances rhodium(III) complexes with 3-pyrazolidone derivatives are the cause of stabilization of positive photographic materials based on AgCl,Br-emulsions containing rhodium, when 3-pyrazolidone derivatives are introduced therein.[53]

Though there are detailed reviews on the stabilization of the silver halide systems,[54,55] the coordination compounds have been paid less attention to, and their potential abilities and mechanisms of action are not clear enough. In cases in the cited work,[3] the stabilizing effect of platinum group metal complexes, in view of their high oxidizing power, can be interpreted in terms of a sort of some "preventive elimination" of fog centres formed during the storage period. To explain the stabilizing effect caused by other complexes,[48] some other considerations are required. The most widely spread coordination compounds are known as stabilizing agents for both silver and non-silver organic dye images. The latter are sensitive to light[2] and fade with time: they fade quite rapidly under exposure to direct sunlight. To inhibit this process, the introduction of various chelate complexes into the photographic layers is practised.[56–70] In a US patent,[56] which is the pioneer work in this field, compounds VII and VIII have been proposed, where M is nickel, cobalt, copper, palladium or platinum, K is an alkali metal, and A is *o*-phenylene, C(=O)C(=O), or CR^1=CR^2 (R^1, R^2: H, phenyl, CN, or alkyl).

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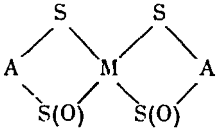
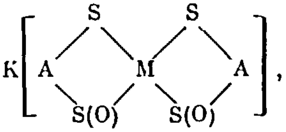


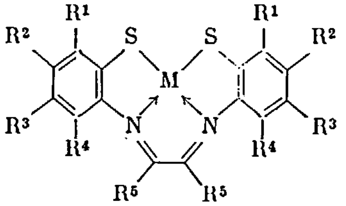
VII



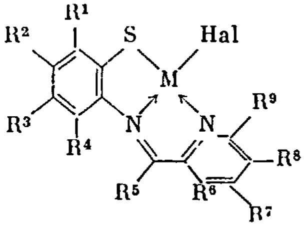
VIII

These chelates have absorption maxima in the visible region which are bathochromically shifted relative to the absorption maxima of the organic dyes forming a colour image.

The list of such stabilizing agents was considerably expanded during the last few years due to works of Japanese and American investigators:[57–62] described are 3d- and 4d-element complexes with heterocyclic nitrogen–sulphur-containing ligands giving five-membered chelate rings, IX–XI, where M is cobalt, nickel, copper, palladium, or platinum, R^1–R^9 are aryl, alkyl, CN, or a heterocyclic group.



IX



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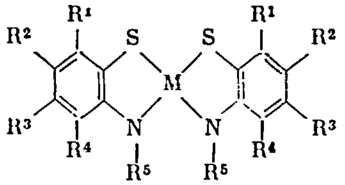
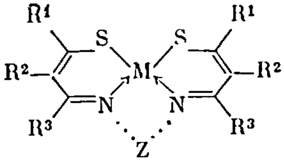


XI

The similar metal complexes forming six-membered chelate rings,[61] XII, and those of the O-donor chelating agents in place of the S-donors,[62,63] XIII and XIV, are reported, where R^1–R^3 are H, alkyl, aryl, CN, or halogen, and Z is a group of atoms for completing a 5- or 6-membered chelate ring.



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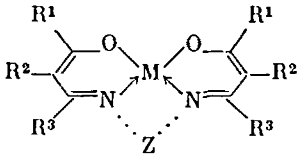

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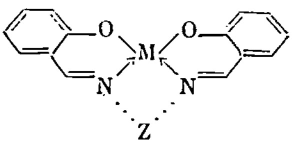
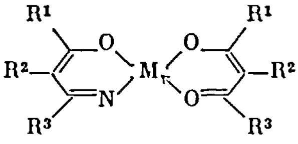


XIV

Structures XV,[64] XVI,[65] XVII,[66,67] XVIII,[68] XIX,[69] and even a heteronuclear nickel–tungsten cluster XX[70] are also employed.



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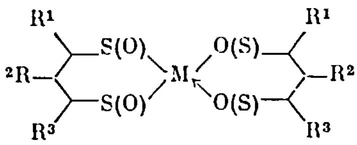

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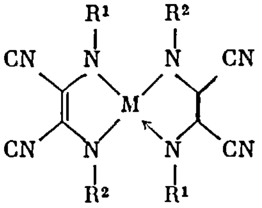
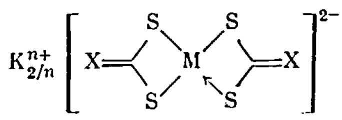
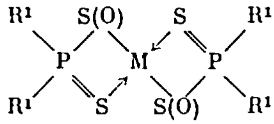


XVII



XVIII



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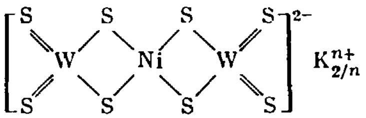

XX

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The range of the sensitizing effect of these chelates is wide enough and covers visible (400–700 nm) and the nearest UV region (up to 300 nm). According to the data available, these compounds cannot be considered as universal ones and work only on the images formed by the dyes of a limited series. The successful use of agents XXI[71] and XXII[72] and other complexes with nitrogen$^-$, oxygen- and sulphur-containing ligands[73,74] for stabilization of silver images against detrimental effects of hydrogen sulphide, oxidants and some other aggressive compounds found in the atmosphere, is described. There are no explanations of this effect; however, it can be suggested that the chelates reported in[71–74] act as traps for aggressive compounds on the surface of a photographic layer and form mixed complexes containing a harmful molecule (or a part of it) in the inner sphere. The argument in favour of this supposition is that cobalt(II) phthalocyanine XXII where cobalt atom is capable of raising its valency and forming additional dative links, is a good image stabilizer compared to a similar copper(II) phthalocyanine compound.

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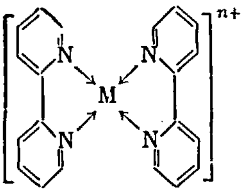
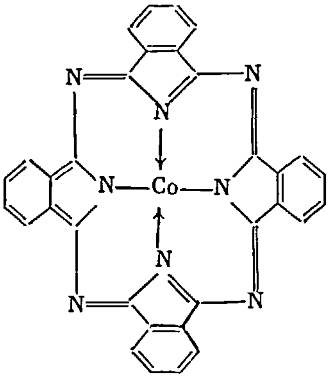


XXI



XXII

The interest for the search of new stabilizing chelate complexes is not relaxed for the last few years[75–90] and more complex coordination compounds containing four chelate rings, particularly those of structures XXIII[77] and XXIV[83] where R^1–R^4 are alkyl or aryl, X is OH, SR^1 or NHR^1, M is nickel, cobalt, palladium, and Y is a bivalent radical such as methylene or phenylene, are involved into an investigation sphere. No supposition has been made on the possible causes of the stabilizing effect of the above mentioned salts and this problem needs further investigation.[90]

2.3. *Coordination Compounds as Antifogging Agents*

There are few works concerning the utility of d-element coordination compounds as antifoggants for the photographic materials.[91–93] There is a certain relationship between stabilization of photographic characteristics of silver halide materials and their antifogging effect that a stabilizer is at the same time an antifogging agent and vice versa.[2,3] A good example of such a relationship are the above mentioned silver(II) complexes containing macrocyclic ligands[35] which prevent fog formation when used even in very low concentrations (0.002–0.005 g/m^2).[91] In this case the antifogging effect of silver(II) chelate complexes is evidently connected directly with their ability to oxidize fog centres rapidly and effectively. Similar mechanisms could be involved to explain the antifogging effect of gold(I) complexes of PR_3AuX

type where R is C_6H_5, C_6H_4Cl, $CH_3OC_6H_4$, or C_6H_5O, X is chlorine, bromine, iodine or CH_3.[92] However, this concept meets considerable difficulties in case of the interpretation of the antifogging effect of various carborane complexes of cobalt, nickel, platinum, silver, etc. of the formulae $(C_2H_5)_2PPtB_3H_7$, $(C_2H_5)_2PPtB_8H_9(B_{10}H_{10}CNH_3)_2Ni$, $(B_{10}H_{10}S)_2CoCs$, $Cs_2Fe(B_{10}H_{10}CH_2)_2$ and the like boron compounds which can be effective in extremely small amounts (10^{-8}–10^{-6} mol/AgHal mol)[93] and within a wide pH range (3–9). It should be noted that coordination compounds described in the Japanese and GDR patent publications[50–52] are effective fog bleaching agents.

2.4. *Coordination Compounds As Hardening Agents*

The earliest example of the utility of a coordination compound as a hardening agent for photographic silver halide materials with a binding gelatin component is a chromium(III) complex.[2,3] The mechanism of hardening has long been known and involves linking the mobile gelatin molecules or their fragments by chromium(III) ions during the formation of 5- and 6-membered rings with donor oxygen, nitrogen or sulphur atoms.

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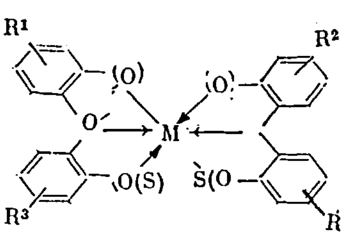
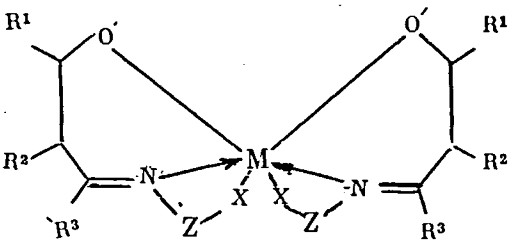
Chromium(III) complexes are still used in practice when the so-called "soft" hardening is desirable.[2,3] but on the whole the range of hardening agents–complexes has increased. Cobalt(III) complexes are used more frequently, though other hardening compounds are known.[94–100] For example, polyvalent metal complexes (aluminium, iron, tin, platinum, thorium, cobalt, chromium) with nitrogen- and halogen-containing ligands are used for better adhesion of a photographic layer to a glass substrate,[94] the result being achieved by treating the substrate with solutions of the above complexes. The photographic materials have been proposed, the gelatin layer of which is hardened during the development by $[Co(NH_3)_6]^{3+}$ or $[Co(NH_3)_5CO_3]^+$ complexes.[95,96] The extent of hardening increases with the amount of silver developed.[96] As hardening agents, other nitrogen-containing cobalt(III) complexes such as those with ethylenediamine and diethylenetriamine are known.[97] A special type of a hardening solution which could be called a "preserved hardening solution" has been proposed by American authors.[98] Titanium(IV), zirconium(IV) or chromium(III) complexes with oxyacids (lactic acid, tartaric acid, citric acid) are introduced into the photographic layer. Taken separately, these complexes do not produce a hardening effect, but upon introducing nickel(II), zinc(II) or cobalt(II) ions into the system, the latter, by means of the more stable complex formation, are substituted for titanium(IV), zirconium(IV) and chromium(III) in the inner coordination sphere, and gelatin molecules are linked in stronger complexes.

In practice, to provide for the realization of this process, a so-called covering layer containing nickel(II), zinc(II) or cobalt(II) salts is coated upon the light-sensitive layer. These salts diffuse into the light-sensitive layer during the development and produce an effect on the multivalent metal complexes contained therein and activate the above discussed mechanism.[98]

As an effective way for hardening photomechanic compositions, organometal complexes of titanium(IV) and vanadium(IV) have been proposed.[99] The metal atoms are linked with carbon atoms of four bicyclic groups (in particular, 1-bicyclo-2,2,1-heptyl groups with an alkalydene group in 2- or 7-position), *e.g.* tetra-*cis*-(camphenyl-1)vanadium(IV) (XXV). For the last few years the search for new hardening complexes is going down, although some data can still be found in literature especially those concerning the use of XXIV type compounds.[100] In general, this aspect of co-ordination compounds in photography is the most developed.



XXIII



XXIV

2.5. *Coordination Compounds as Catalysts or Inhibitors of Crystal Growth*

The works of Bulgarian investigators headed by Todorova[101-105] are of obvious interest. In these works the possibility of employment of 3d-element coordination compounds as catalysts or inhibitors of silver halide microcrystal (MC) growth in the course of physical ripening is reported. In the earliest paper[101] the influence of copper(II), iron(II), mercury(II) and thallium(I) complexes with EDTA on the growth rate and habitus of silver bromide octahedral microcrystals was investigated at $pH = 6.0$, $pBr = 2.3$ and $T = 65°C$. As it has been shown, iron(II) complexes do not substantially affect the MC growth rate, while thallium(I) and mercury(II) complexes at first accelerate and then inhibit the growth rate. On the contrary, the increase of copper(II) complex concentration accelerates the MC growth rate compared to that without any complexes. They suggest that the acceleration of MC growth is connected with blocking active fragments of gelatin molecules with which gelatin is adsorbed on the MC surface (amino-, carboxy- and carbamide groups), while the inhibition of its growth is interpreted as a result of adsorption of metal ions or their complexes on certain MC faces, which leads to a change in their habitus.

In the later work[102] it has been shown that lead(II), zinc(II) and cobalt(II) complexes of XXV type produce a slight effect on the MC growth of AgCl(Br)-emulsions, provided that the effect of the latter is strongly dependent on pH. It is characteristic that EDTA–copper(II) as well as EDTA–cadmium(II) complexes at high pBr values produce an inhibiting effect on MC growth,[103] opposed to the data reported by Todorova and co-workers.[101] However, the inhibiting effect of mercury(II) complexes remains unchanged in this case. The increase in light sensitivity and contrast is observed when EDTA–zinc(II) and –lead(II) complexes are introduced into the photographic material. This is probably connected with a certain growth in size of silver halide microcrystals.[104,107] The authors themselves attribute it to a slight reducing effect of EDTA-complexes on silver halides which seems doubtful in our opinion. It is of interest that the introduction of copper(II) and cadmium(II) complexes into a silver halide emulsion during physical ripening results in equalization of MC size and habitus,[105] which is of practical importance in some cases. There are no data available on the effect of other complexes on the physical ripening process, except that simple and mixed cyano complexes, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_5NOS]^{4-}$, $[Fe(CN)_5SO_3]^{5-}$, $[Co(CN)_6]^{4-}$, $[Mo(CN)_6]^{4-}$ etc. have been proposed as highly efficient inhibitors of MC growth.[106] The authors

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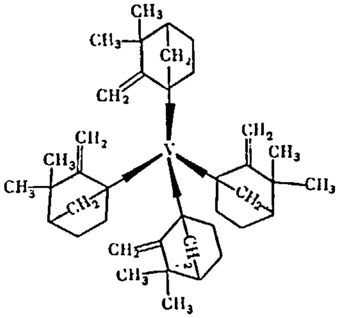
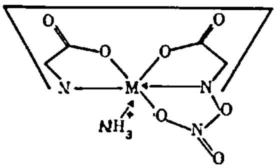
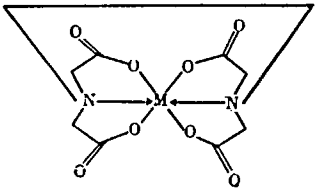
point out the increase in colloid stability of the photographic systems as well as in light sensitivity when the inhibitors are combined with optical sensitizers which can be used for the preparation of high resolution photographic layers for holography. To inhibit the growth rate of silver halide microcrystals effectively, the employment of metal complexes belonging to the platinum group has been proposed;[108,109] they are rather effective in the concentration range from 10^{-7} to 10^{-5} mol/mol of silver halide.



XXV



XXVI



XXVII

3. COORDINATION COMPOUNDS IN CHEMICAL-PHOTOGRAPHIC PROCESSING OF SILVER HALIDE MATERIALS

Conventional chemical-photographic processing of silver halide materials comprises the development (reduction of silver halide in the exposed areas) and the fixation (dissolution of unreacted silver halide).[2,4,110] In the case of colour photographic materials, there are the following stages such as development (reduction of silver halide with simultaneous dye formation), bleaching (the transformation of silver into silver halide or some other compounds) and fixing.[2,4]

3.1 Coordination Compounds in Development Processing

It can be suggested that at the first of the above stages, complexes can be used either as reducing agents for silver halide, or as accelerators of the development process. Vanadium(II) complexes with bromide ions[111] and iron(II) potassium oxalate, $K_2[Fe(C_2O_4)_2]$,[112] were the first compounds to be used as developers, discovered in 1868 and 1877, respectively. Later on metal complex compositions with metals being in their lower valence states such as chromium(II),[113,114] ruthenium(II),[114] titanium(II),[115-118,120] titanium(III),[119-121], vanadium(III),[120-122] iron(II),[122-124] vanadium(II),[125-127] molybdenum(III) and tungsten(III)[113] with various oxygen- and nitrogen-containing ligands, particularly with complexons, have been proposed.

The investigations performed have shown that compositions having similar active agents are capable of developing silver halide layers in the wide pH range from 1 to 10. The most widely spread are Fe(II) complex compositions with various ligands including exotic ones such as "sandwich compounds" XXVIII,[110] though there is evidence of good potential abilities of other d-element complexes.

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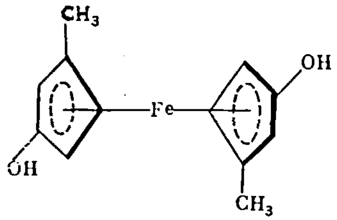

XXVIII

For example, for vanadium(II) complex developers, no induction period is observed, which is characteristic of conventional developing agents such as methol and hydroquinone as well as the high level of silver halide reduction.[125,126] These compounds could be reduced by electrochemical treatment and thus be used in continuous processing units.[127] The mechanism of the developing effect is not yet well known. According to Sheppard and Mees,[128] the effect of a ferrous oxalate developer[112] can be described by the following equations:

$$Ag^+ + [Fe(C_2O_4)_2]^{2-} \longrightarrow Ag + [Fe(C_2O_4)_2]^-$$

$$[Fe(C_2O_4)_2]^- + C_2O_4{}^{2-} \longrightarrow [Fe(C_2O_4)_3]^{3-}$$

The investigation of $[Fe(C_2O_4)_2]^-$ at $pH = 5.8$ on a silver electrode has shown a diffusion-limited single-electron transfer reaction,[107] Apparently, ferrous complexes containing oxyacids such as lactic acid, citric acid, tartaric acid, and salicylic acid work in a similar way. The composition containing edta-iron(II) complex is considered to be one of the most effective ferrous developers. The standard potential of the $[Fe(edta)]^- \rightarrow [Fe(edta)]^{2-} + e$ pair relative to a calomel electrode is equal to + 0.117 V. The ability of such developers for oxidation in the air increases with pH. The development rate at first increases reaching its maximum at $pH = 4{,}0$ and then it decreases.[130] The electrochemistry of this system has been investigated in detail.[131] The recovery of exhausted iron(II) compositions is possible by means of electrode membranes.[132]

Certain considerations about electron transfer mechanism in homogenous aqueous media can be applied to heterogeneous development by d-element complexes. The works of Price[114,133] have been written in this key where the mechanism of development by chromium(II), ruthenium(II) and titanium(III) complexes with various nitrogen- and oxygen-containing ligands are discussed. It has been shown that fog formation is the result of reactions involving the outer sphere, while image formation can be considered as the reaction of both the outer $[Ru(NH_3)_6]^{2+}$ and inner spheres (edta-chromium(II) and titanium(III) complexes). The similar mechanism is suggested for the developer containing diethylenetriaminepentaacetazide-titanium(III) complex.[121] It is likely that in all similar cases fog formation is the result of the involvement of the outer sphere only. According to the data cited, the development rate is determined first of all by a redox potential of the developer active agent and very seldom is it conditioned by diffusion factors.

Another possible field of application of coordination compounds in the development process is the acceleration or inhibition of this process in compositions based on conventional developing agents (methol, hydroquinone, etc.) which is presented in patents only. Octahedral ruthenium(III) complexes have been suggested which

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contain various uni- (NH_3, SCN^-, Cl^-, etc.) and bidentate (ethylene- and triethylenediamine) ligands.[134] Upon the introduction of the above complexes in the amounts of 10^{-5}–10^{-4}mol/l into the developers containing polyoxybenzole, pyrimidine or hydroxylamine, a sharp decrease in the introduction period and increase in optical densities of images obtained with long exposure times, are observed. The authors suppose that ruthenium complexes form a reduction–oxidation pair between a developer and silver halide. Firstly, the ruthenium(III) complex oxidizes the developing active agent, and secondly, its reduction product, ruthenium(II) reduces silver halide to metallic silver. It should be noted that notwithstanding the possibility of existence of such a catalytic mechanism, it is in poor agreement with the similar effect of chromium(III) complexes[135] for which the transition of chromium(III) to its lower oxidation state is hardly probable. In the paper cited,[135] pseudooctahedral palladium(II), platinum(II), iridium(III), rhodium(III), cobalt(III) complexes containing EDTA and derivatives thereof are reported as development catalysts which are introduced in very small amounts. It is interesting to note that kinetically inert complexes having d^3- and d^6-configurations produce the highest catalytic effect. This phenomenon, however, has not been discussed yet. The inhibiting effect has been observed for copper(II), nickel(II) palladium(II), gold(III), rhodium(III) and platinum(II) complexes with mercaptotetrazols, mercaptothiadiazoles and mercaptoimidazoles.[136] It is characteristic that development inhibition is observed upon the introduction of the above complexes both into the developing solution, and into silver halide emulsions.[136]

Fast developers containing amidol, glycine, phenidone and a small amount of ferrous complexes with EDTA or a diethylenetriaminepentaacetic acid have been described. The complex stabilizes the composition against oxidation (due to this effect, the developers remain stable in the open air). Another useful property of coordination compounds is their desensitizing effect which enables one to develop photographic layers in red or even yellow light due to the low sensitivity of materials to visible light. It is admitted that square planar d-element complexes,[137] can be used as desensitizers. At least one case can prove it when a palladium(II) thiosemicarbazide complex XXIX is used.[139]

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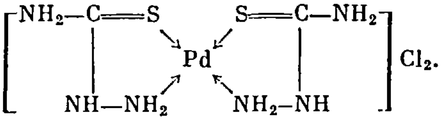
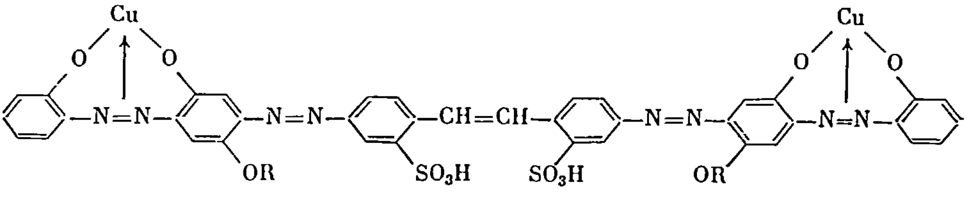


XXIX

There are also data on the activating effect of $[Fe(CN)_6]^{4-}$, $[Cr(EDTA)]^-$ and $[Co(NO_2)_6]^{3-}$ in the developers containing 7-me-thylacenaphtho(1,2-b)quinoxaliniummethylsulphate as a desensitizer[140–142] as well as methol-hydroquinone developer with an antifogging tetra(5-nitrobenzimidazole)palladium(II) dichloride for X-ray film processing.[143] There are very few works in this field; no analytical presentations can be found either.

3.2. Coordination Compounds in Bleaching Processes

The earliest example of application of coordination compounds in bleaching compositions is potassium ferricyanide, $K_3[Fe(CN)_6]$.[2,4] This compound is highly toxic and the search for its substitute is still actual.[4] For the last few years ferric complexes were most frequently used in bleaching and bleach-fixing systems.[144–157,162,168–177] cobalt(III) complexes were rarely used,[158–166] and copper(II) complexes still more rarely used.[162,167–172] As far as other metal complexes are concerned, there were only isolated cases of their application. The most widely used bleaching agent is EDTA-ferric complex.[144–149,150–152,155–157,162,170,171,176,177,182–192,194] This compound has a number of advantages such as complete bleaching of silver even in the areas with a high metal concentration, the absence of fog and toxic properties. There are some data on the employment of ferric complexes containing aminopolycarboxylic acids[154,186,188–191] and oxyacids[151,153,173–175] which are however less stable in the light, though more effective compared to Fe(edta) bleaching solutions.[151] During the last few years, cobalt(III) complexes attracted a steady attention due to a number of advantages compared to ferric bleaching compounds, such as a higher resistance to light, a compatibility with sodium thiosulphate; in contrast to ferric complexes, those of cobalt(III) are not reduced by sodium thiosulphate to bivalent state. The complexes with uni- and bidentate nitrogen-containing ligands (NO_2^-, NH_3, SCN^-, ethylenediamine)[160] and heterocyclic ligands with a nitrogen atom in the nucleus[166] are used more frequently. Cobalt-(EDTA) has also been described as an oxidant.[165] Some authors prefer bleachers containing copper(II) complexes as the principal agent. For example, a dimeric complex with the formula XXX (R: alkyl) has been proposed.[167]



XXX

It is also known that $[Cu(edta)]^{2-}$ bleacher combined with 3,5-dioxybenzoic acid or 2,6-dioxynicotinic acid works quite well, providing for a high homogeneity of bleaching without any fog or spots.[167,171]

Extremely promising bleachers are known for the diethylenetriamine–copper(II) bleaching systems working in the pH range from 3 to 9, and compounds of the general formula $RN(CH_2PO_3Cu)_2$ where R is aryl, alkyl, or aralkyl. These copper(II) complexes are particularly useful for bleaching photographic layers containing colour couplers of the phenol or naphthol type.[168] It is worth mentioning that bleaching of silver by iron(III) and copper(II) nitrate solutions is accelerated in the presence of phenosafranine and methylene blue.[169] Probably the iron(III) and copper(II) complexes formed with these organic dyes have a better bleaching effect. In some cases the bleaching of silver by compositions containing $[Fe(edta)]^-$ as an active agent is catalyzed by a number of d-element complexes such as those of iron(II), cobalt(II), nickel(II), copper(II), palladium(II), platinum(II), silver(I), and gold(I), ligated with selenourea and selenosemicarbazide, as well as their *N*-substituted derivatives.[148] Other complexes are also used for this purpose.[152,193] It should be noted that the bleaching solution containing $K_3[Fe(CN)_6]$ as an oxidizing agent and palladium(II) chelate with 5-methyl-7-oxy-1,3,4-triazaindolycine can be used as an inhibitor of silver fog.[193] This inhibitor is capable of not only substan-

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tially decreasing silver image densities uniformly over a wide range, but also of eliminating fog.[193]

The chemistry of processes in bleaching and bleach-fixing compositions has been investigated only in a few papers for (ethylenediaminetetraacetato)ferrate(III) systems.[179-181] Two reactions are pointed out to decrease simultaneously both oxidative activity and diffusion coefficient of $[\mathrm{Fe(edta)}]^-$:[179,180]

$$[\mathrm{Fe(edta)}]^- + H_2O \longrightarrow [\mathrm{Fe(edta)OH}]^{2-} + H^+$$
$$2[\mathrm{Fe(edta)OH}]^{2-} \longrightarrow [\mathrm{(edta)Fe{-}O{-}Fe(edta)}]^{4-} + 2H^+$$

In bleach-fixing compositions the similar dimerization takes place along with a redox reaction.

$$2[\mathrm{Fe(edta)}]^- + S_2O_3{}^{2-} \longrightarrow 2[\mathrm{Fe(edta)}]^{2-} + S_4O_6{}^{2-}$$

which leads to a loss of bleaching and fixing abilities of a solution relatively soon.[181]

3.3. *Coordination Compounds in Fixing Processes*

Though the fixing process itself is closely connected with a complexation reaction,[2,4] coordination compounds offer a few possibilities which are mostly confined to catalysis. For such purposes, selenocarbazide complexes of 3-d elements[195] and edta-complexes of cobalt(II), manganese(II), zinc(II), palladium(II), and cadmium(II)[196] have been proposed. In one of the recent papers[197] a mixed hetero-ligand zinc(II) complex containing edta and nitrilophosphoric acid in the inner sphere has been proposed. The mechanism of such a catalytic activity of the above complexes is not clear yet, and there are still no publications on this subject.

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4. COORDINATION COMPOUNDS IN ADDITIONAL PROCESSING OF SILVER HALIDE PHOTOGRAPHIC MATERIALS

Additional processing of silver images usually pursues one of the aims as follows: 1) intensification (increase in optical densities), 2) toning (dyeing), and 3) protection from surface oxidation. Other fields of application of additional processing which are of no practical importance[2,4,198] will not be discussed here.

4.1. *Coordination Compounds in Image Intensification Processes*

Speaking of image intensification, two possible methods should be pointed out: one is the intensification with catalytic precipitation of other metals, usually less noble than silver, on the silver image, the other being that accompanied by other processes. The former method is called "physical development", for which the contribution of coordination compounds has been described in detail.[1] Here will be discussed for the latter method.

A number of intensifying systems of this type in which complexation plays a decisive role has been described.[4] A representative example is a two-solution copper intensifier where the active agent of the bleacher is $[\mathrm{CuBr_4}]^{2-}$ anion and a "blackening solution" is composed of various ammoniacal silver(I) complexes. An image intensified by 2–3 times is obtained upon processing in this solution, but the image formed has a poor storability.[4]

Single-solution type uranium and cobalt intensifiers are also known, $K_3[Fe(CN)_6]$ being the active agent in both. In the uranium one the following reaction takes place:

$$Ag + K_3[Fe(CN)_6] + 2UO_2(NO_3)_2 \longrightarrow 2(UO_2)_2[Fe(CN)_6] + 3KNO_3 + AgNO_3$$

The optical density and gamma are observed to increase by two or three times. The image obtained has brick-red colour and consists of uranyl(VI) hexacyanoferrate(II) only.[199,202] This intensifier produces a strong fog and therefore is rarely used in practice. An intensifier containing $K_3[Fe(CN)_6]$, cobalt(II) chloride, citric acid and its 3-substituted potassium salt, has been proposed by Kolosov.[201] According to Kirillov,[4] its reaction mechanism can be described by the following scheme:

$$2Co_3[Fe(CN)_6]_2 + 4Ag \longrightarrow Ag_4[Fe(CN)_6] + 3Co_2[Fe(CN)_6]$$

Such an interpretation is somewhat doubtful, since upon the intensification the image acquires a violet-brown colour, while cobalt(II) hexacyanoferrate(II) is green.[203] There are data on the successful employment of this compound for intensifying track images in the so-called "nuclear photographic materials".[200] Intensifiers obtained on the basis of cobalt(III) complexes are characterized by a comparatively poor storability.[209] Nevertheless, they have attracted an unusual degree of interest from investigators due to their efficiency in the so-called catalytic dye formation process.[29,30] A great number of works dealing with this problem have been published for the last few years.[204–214] From the view-point of the chemistry of coordination compounds, the most interesting is the effect of the nature of outer- and inner-spherical acido-ligands in ammine–cobalt(III) complexes on their efficiency upon the catalytic formation of dyes.[206,207] In particular, the activity of complexes of $[Co(NH_3)_{6-n}(NO_2)_n]^{(3-n)+}$ type ($n = 0$–4, 6) is observed to decrease with decrease of the charge, and the *cis*-isomers have a higher activity than the *trans*-isomers.[207] This phenomenon may be associated with the differences in thermodynamic or kinetic stabilities of these complexes.[207]

A number of works[205,208,212–214] are dedicated to the study of the reaction mechanism of catalytic dye formation. According to the above works, a conclusion could be made that elemental silver reduced by a colour developing agent such as *p*-phenylenediamine is oxidized upon the reaction with the cobalt(III) complexes into silver halide, which is later re-reduced by a new portion of the developing solution to elemental silver, etc. As a result, the content of an oxidized form of a colour developing agent in the system is increased, providing for the increase in the amount of the dye formed, which in turn forms a colour image. The modern state of affairs for this particular problem is shown rather well in a review.[211]

Lately, an intensifier has been proposed by which the silver image is reduced in the solution containing mixed tin(II) hydroxotartrate complex. The interaction results in an unusual "overprecipitation" of silver with the formation of a dark-brown or red image.[215] Such an intensifier, in contrast to cobalt complexes, is quite stable and provides for a very good reproducibility of results. For the last few years, the processes of silver image intensification which involve the transformation of silver images into non-silver ones have been developed. Carriers for such non-silver images employed are iron(III), copper(II) hexacyanoferrate(II),[216–219] intensively coloured dithiooxamide chelates of cobalt(III),[220,221] nickel(II),[222–224] and copper(II),[225]

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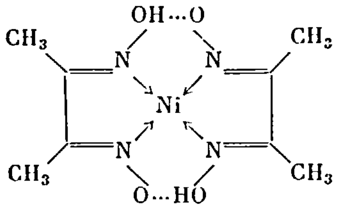
nickel(II) complexes of *N*,*N'*-diphenyldithiooxamide[226] and dimethylglyoxime,[227] and copper(II) complexes of bis(thiocarbamoyl)hydrazine.[227] In certain cases, owing to these processes, the sensitivity of the material can be increased by 5–10 times and even more.[221,225]

4.2. Coordination Compounds in Toning Processes

There are several ways of image toning which are closely related to intensification methods, as far as their effects and final results are concerned.[4,199] In a number of cases a toner can act as an intensifier and vice versa. Most of the toning systems are two- or multistaged, single-solution systems being quite rare.[4,199,202] In the latter case such a solution usually contains potassium hexacyanoferrate(II), a soluble metal salt, and an oxyacid or its alkali salt. Processes of silver bleaching and precipitation of intensively coloured hexacyanoferrate(II) complexes on the image are combined in one.[228] However, these compositions are unstable and become completely inactive within a few days. Thus, in practice, frequently used are the systems in which bleaching and dye formation take place in different solutions and at different times.[4,228] The image toning is connected with the precipitation of less soluble hexacyanoferrate(II) complexes of iron(III) (blue toning), copper(II) (red-violet toning), and uranium(VI) (green toning). However, there are examples of dyeing due to the formation of brightly coloured d-element chelates: *e.g.*, bis(dimethylglyoximato)nickel(II),[227–229] **XXXI**, α-benzoineoxymato-diaquacopper(II),[230] **XXXII**, and bis(dithiooxamido)nickel(II),[223,224,227,231] **XXXIII**, produce the images of a purple, yellow green, and blue colours, respectively. The last system is recommended for the production of popular "blue transparencies".[231] Additionally, an amber colour-dyed image is given with cobalt(III)–dithiooxamide,[220,221] red with cobalt(II)–(2-nitroso-1-naphthol),[232] dark-green by copper(II)-dithiooxamide,[225] and red-violet with nickel(II)-*N*,*N'*-diphenyldithiooxamide.[226] Upon the completion of the treatment, silver is completely removed from silver halide photographic material processed.[227] The most important fact is that non-silver images obtained by the above techniques have an extremely high light resistance and do not fade during storage.



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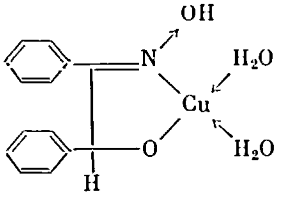
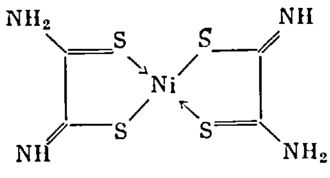


XXXII



XXXIII

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In general, the complexation mechanisms in toning systems can be regarded as established ones.[4,227,228] However, the composition of complexes in bleach-toning solutions and their transformation during decomposition of the latter under storage conditions are not clear yet. Therefore, the stability of these systems has not been improved. This instability is in part obviously connected with the photolysis of $K_3[Fe(CN)_6]$. The decisive stage for the formation of photographic characteristics of a non-silver image is toning.[220-234] From the view-point of chemistry, this stage is a complexation process of d-element hexacyanoferrates(II) and various chelating ligands.[227,233,234] Systematic investigations of such processes have been started recently.[223,234] It has been found that the complexation reaction of nickel(II) hexacyanoferrate(II) with nitrogen–sulphur-containing ligands can lead to not only the formation but also the destruction of a non-silver image. Such a phenomenon is clearly demonstrated upon the synthesis of non-silver images obtained from nickel(II) chelates of dithiooxamide.[233] The formation of ferrous chelates is sometimes affected by air-oxidation in an alkaline medium.[234] The investigation of these processes lacking for silver is of theoretical and practical importance now. The above-mentioned method of image processing, which is accompanied by both intensification and complete removal of silver from the photographic layer, provides for additional reserves of saving of this precious metal.

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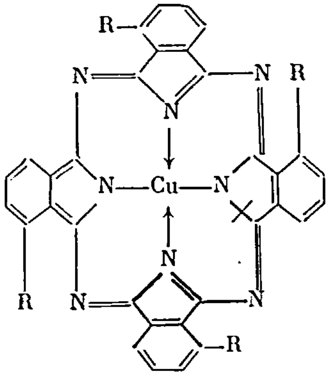
4.3. Coordination Compounds for Protection from Surface Oxidation Processes

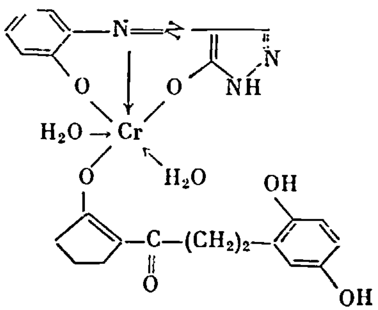
The last of the items under discussion is the protection of images from destruction during storage; it is achieved by the precipitation of noble metals such as gold and platinum on the image. This process has been known for a long time,[4] and has not changed much until now. It comprises silver image processing with $Na_2[PtCl_6]$, $H[AuCl_4]$, or $NH_4[Au(SCN)_2]$ solutions which produce a thinnest gold or platinum protecting layer. It is worth mentioning that simultaneous brown, violet, or blue-black toning of images is carried out.[4,200] However, little attention has been paid to this matter, in spite that the stability of silver images is still a grave problem.

5. d-ELEMENT COORDINATION COMPOUNDS AND COLOUR DIFFUSION PROCESS

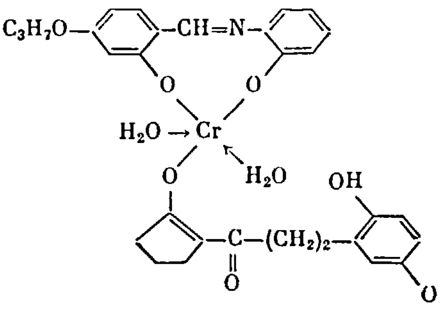
In 1947 an American inventor E. Land proposed a single-stage colour photographic process including simultaneous chemical-photographic processing of an exposed film and the formation of a positive image. Leaving technical details apart, it should be noted that the image obtained by means of so-called "colour diffusion process" or "instant photography" contains no silver at all and consists only of brightly coloured 3d-element chelates. In spite of a number of disadvantages, such as high cost, problems in manufacturing materials and production of cameras, impossibility of picture reproduction, etc., this process has widely spread in the world due to its high operation and high image stability compared to conventional colour materials; chelate complexes forming an image are more light-resistant than organic dyes.[235-275] At present the most popular version of this process is such that magenta and yellow dyes are represented by chromium(III) complexes of azo- or azomethine dyes and the blue dye by template copper(II) complexes of substituted phthalocyanines.[235-245] The typical complexes used are those of general formulae XXXIV–XXXVI where R is $SO_2MHCH(CH_3)CH_2C_6H_3(OH)_2$.[237]



XXXIV



XXXV



XXXVI

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In SX-70 Polaroid (USA) the above or similar compounds are used.[241] Most likely, this combination is the most useful to obtain colour images. As magenta and yellow dyes, chromium(III) and other complexes have been proposed,[246–252] but they have not spread so widely. Of academic interest is the suggestion[253] to use nickel and cobalt analogues of compound XXXIV as a blue dye; nickel(II),[254–258,266,268,271] palladium(II),[256–261,266,274] cobalt(III) and rhodium(III)[259] complexes of a wide variety of nitrogen–oxygen-containing chelating ligands are also proposed for various application purposes. As a light-sensitive agent, silver(I) halide is usually used in these processes, though there is some evidence of the use of other silver(I) compounds, e.g., those of dithiooxamide,[260] 4-amino-1,2,4-triazolinethion-5 or its derivatives[261] as well as disulphide of $HOOCR^1SSR^2COOH$ type where R^1 and R^2 are alkylene or arylene.[262] Finally, the introduction of silver(I) complexes containing bis(dimethylcarbamoyl)sulphide into the photographic material to obtain "instant radiography" has been proposed.[263] A wide range of coordination compounds can be used in colour diffusion process.[264] The chemistry of non-silver image formation in these systems is discussed in detail in two reviews.[270,275]

Summarizing the above considerations, one can make at least three main conclusions:

First: there are no such fields of application of a silver halide process where coordination compounds are not widely used; second: a greater part of works on the subject is presented in patents, the investigations performed having a distinctly pragmatic character; third: the data available on the problem are quite fragmentary and seldom discussed by the authors. As for the third it is very difficult or even impossible to make up a comprehensive narration of the scattered data. However, the field of coordination chemistry discussed here presents an obvious theoretical and practical interest and deserves a steady attention on the part of specialists in coordination chemistry.

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