

HgCl₂ based materials for X-rays recording

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Studies of polyvinyl alcohol/mercuric chloride films have been carried out including quantum-chemical calculations of energy structure, potential surfaces of the ground, excited, and ionized states of mercuric chloride as well as of complexes formed by the mercuric chloride decomposition products with ammonia. The irradiation of film with high-energy quanta (about 3 keV) followed by ammonia vapor exposure results in an image appearing. It is the mercuric chloride molecule excitation into the dissociative state by secondary electrons followed by dissociation that has been shown to be most likely mechanism of the radiation-chemical process. The optical contrast is provided due to formation of Hg₄(NH₃)₄Cl₂·H₂O complex in the film and to condensation, under irradiation, of mercury microdroplets scattering light and giving rise to imaging effect similar to the vesicular one.

Проведены исследования пленок поливиниловый спирт/сулема HgCl₂, включающие квантово-химические расчеты энергетической структуры, потенциальной поверхности основного, возбужденного и ионизированного состояния сулемы, а также комплексов продуктов распада сулемы с аммиаком. Облучение слоев высокоэнергетическими квантами излучения (~3 кэВ) с последующим выдерживанием в парах аммиака приводит к появлению изображения. Показано, что наиболее вероятным механизмом радиационно-химических процессов является возбуждение молекулы сулемы вторичными электронами в диссоциативное состояние с последующей диссоциацией. Оптический контраст достигается за счет образования в пленке комплекса Hg₄(NH₃)₄Cl₂·H₂O и конденсации в условиях облучения микрокапель ртути, рассеивающих свет и вызывающих эффект изображения типа везикулярного.

To establish the regularities of radiation-induced processes occurring in a substance subjected to various ionizing radiation kinds is a problem of importance in the radiation materials science [1]. This problem is complex and difficult to solve. That is why the known results obtained in studying of the radiolysis stages do not always make it possible to forecast quantitatively (and even qualitatively in some cases) changes in macroscopic properties of materials caused by irradiation. This is due to the lack of reliable data on mechanism and kinetics of radiation-induced processes as well as of quantitative models describing the change character for specific properties of compounds and materials based thereon [2].

Before, the authors reported a novel X-ray sensitive silver-free material consisting of a polyvinyl alcohol [-C₂H₄O-]_n layer containing mercuric chloride HgCl₂ [3, 4]. It has been found that irradiation of such films with high-energy quantum followed by exposure in ammonia vapor results in formation of a black product that is a prerequisite for data recording using the radiation. Processes occurring in the material under irradiation and during storage have been postulated. Some difficulties, however, were discovered. The image was found to be rather unstable; the material has shown a low sensitivity; the physical processes taking place in the layers under X-ray irradiation

tion were not conceived sufficiently to improve the material photographic characteristics.

Since it is just electron transitions in the UV region that are typical of the compounds involved in the processes under consideration, investigations in this field are necessary to study the energy conversion mechanisms in the molecules, especially, in HgCl₂ one that plays the main part in the mentioned processes. The molecular structure of mercury halides is well known [5–7], but the information on radiation sensitivity mechanisms of those compounds is incomplete. In this connection, it is necessary to calculate the energy structure of HgCl₂ molecule as well as study theoretically and experimentally its UV absorption spectrum and radiation sensitivity of HgCl₂ containing layers. In [8], such a calculation was carried out without taking *d*-AO into account. The calculated results are in a rather good agreement with experimental ones. Some inconsistency between theoretical results and experiment supposes that there are some aspects that are not taken into account, including the effect of *d*-AO of atoms involved in the molecule.

The radiation-induced effects were studied using thin (about 100 μm) films consisting of 10 % (mass) HgCl₂ and 90 % polyvinyl alcohol. The samples were irradiated through a thick perforated metal mask using a 50 kV X-ray tube. To develop the image, the irradiated film was exposed for several minutes in ammonia vapor. The absorption spectra of aqueous solutions and polymer layers containing HgCl₂ were taken in the 185 to 300 nm range (Specord M-40). To study the radiation-chemical mechanisms [9], quantum chemical calculations were carried out using MNDO, MNDO/*d*, PM3, AM1 methods (self-consistent field with configurational interaction) [10–14]. The MNDO/*d* technique provided results most close to experimental ones.

The transparent colorless HgCl₂ containing polymer films of 0.05 to 0.15 mm thickness showed UV absorption bands peaked at λ = 232 nm and λ < 200 nm. The irradiated samples exposed in ammonia were black. If a sample was irradiated for less than 15 min, the image obtained by ammonia exposure was disappeared in time. The repeated exposure of the X-ray sensitive layer in ammonia vapor resulted in restored image. If the irradiation duration ex-

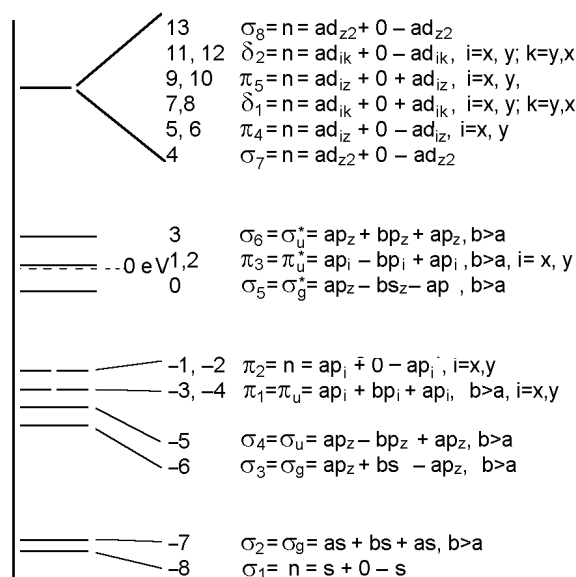


Fig. 1. Energy structure of HgCl₂ and molecular orbital structure.

ceeded 15 or 20 min, the image developed in ammonia was even intensified in time.

To interpret the experimental results, let the energy structure of molecules under study be considered first of all. Then, the short and prolonged irradiation time ranges will be considered according to two time regions of radiation-induced processes occurring in the layers.

The energy structure of Cl–Hg_n–Cl molecules and their complexes with ammonia. The energy structure of mercuric chloride is presented in Fig. 1. The molecular orbitals (MO) with negative numbers are fully occupied with electrons, those with positive ones are empty. It follows from this Figure that the deep 1σ_u state (MO No.–8) is not involved in the chemical bond formation, since it is presented by superposition of chlorine *s*-atomic orbitals (*s*-AO) only. Thus, it is a nonbonding MO (*n*-MO). Similarly, the higher occupied 1π_g-MO (Nos. –1 and –2) are also nonbonding. The atoms are bound in the molecule by four bonding MOs (–3 through –6) where two upper MOs are 1π_u ones while the rest, 2σ_g-MO formed due to interaction of *p_z*-AOs of chlorine and mercury (see Fig. 1). The MOs are presented as linear combination of AO in the atomic ordering in the molecule. The corresponding linear combinations are presented without taking the weight factors into account.

In our case, the *d*-orbitals of chlorine atoms are displayed rather well forming σ-, π-, and δ-orbitals from 4th to the 13th one

(Fig. 1). All of those are, however, non-bonding ones (a slight overlap between distant AO of chlorine results in an insignificant level split).

The experimentally observed absorption band peaked at $\lambda = 232$ nm (the MNDO/*d* calculation gives $\lambda = 230.7$ nm, $f = 0.27$) answers to the quantum transitions between $2\sigma_u$ and $3\sigma_g^*$ MOs, that is, it is related to the $S_0 \rightarrow S_3$ ($2\sigma_u \rightarrow 3\sigma_g^*$) absorption of mercuric chloride. This quantum transition is allowed in dipole approximation. The dipole moment of the quantum transition, as obtained using PM3 and AM1 methods, is perpendicular to the molecular axis and equal to 5.9 D (PM3) or 6.5 D (AM1). In the case of MNDO/*d*, the components of the quantum transition dipole moment are as follows (D): $x = 2.0459$; $y = 1.3960$; $z = -2.7683$. Theoretical wavelength of the corresponding quantum transition ($\lambda = 295$ nm, PM3) is somewhat overestimated due to specificity of semi-empirical PM3 method. The use of AM1 gives a result ($\lambda = 212$ nm) close enough (although not sufficiently) to the experimental value. The MNDO method gives $\lambda = 186.3$ nm for the band mentioned while taking into account *d*-orbitals (in MNDO/*d*) it is possible to obtain the value coincident essentially with the experiment. In the latter case, two first quantum transitions answer to absorption bands at 342.6 nm ($1\pi_g \rightarrow 3\sigma_g$, oscillator strength $f = 0$) and 299.4 nm ($1\pi_u \rightarrow 3\sigma_g$, $f = 0.007$).

The molecular electron configuration in the ground state is as follows: $(1\sigma_u)^2(1\sigma_g)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_g)^2(3\sigma_g)^0(2\pi_u)^0(3\sigma_u)^0(4\sigma_g)^0(3\pi_u)^0(\delta_g)^0(2\pi_g)^0(\delta_u)^0(4\sigma_u)^0$, the $^1\Sigma_g$ state being corresponding thereto. The excited $(1\sigma_u)^1(3\sigma_u)^1$, $(1\sigma_g)^1(3\sigma_g)^1$, $(2\sigma_g)^1(3\sigma_g)^1$, $(2\sigma_u)^1(3\sigma_u)^1$, $(1\pi_u)^1(2\pi_u)^1$ states (6 configurations altogether) have the same

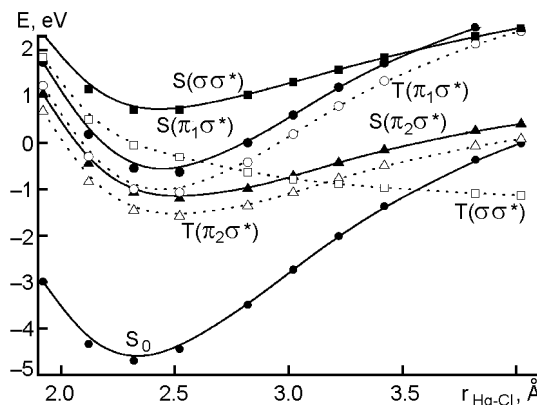


Fig. 2. Energy states of HgCl₂ as functions of the dissociating Hg-Cl bond length.

symmetry. The configurational interactions between those is taken into account in the MNDO method to calculate the electron system energy in ground state. When using MNDO/*d*, along with the above configurations, those created due to taking into account *d*-AOs are considered, namely, $(1\sigma_u)^1(4\sigma_u)^1$, $(1\sigma_g)^1(4\sigma_g)^1$, $(2\sigma_g)^1(4\sigma_g)^1$, $(2\sigma_u)^1(4\sigma_u)^1$, $(1\pi_u)^1(3\pi_u)^1$, $(1\pi_g)^1(2\pi_g)^1$, (12 configurations altogether). This consideration specifies more accurately the energy of atomic bonds in the molecule.

When the molecule undergoes the $(2\sigma_u) \rightarrow (3\sigma_g)$ excitation, $^1\Sigma_u$ symmetry state is formed. Five configurations answer to that symmetry in MNDO method while 11 ones in MNDO/*d*. The calculated results are presented in Table 1 where only quantum transitions are shown corresponding to the spectral range studied herein.

It follows from Fig. 2 that the potential surface of triplet state formed as a result of the $(2\sigma_u \rightarrow 3\sigma_g^*)$ quantum transition is lowered considerably and crosses the potential surfaces of all other excited states as one of Cl-Hg bonds becomes elongated.

Table 1. Quantum transitions in HgCl₂ molecule calculated using MNDO/*d* method

Molecular excitation	Quantum transition	Transition type	λ , nm	Oscillator strength
$S_0 \rightarrow T_1$	$\pi_2 \rightarrow \sigma_5$	$n \rightarrow \sigma_g^*$	383.0	0
$S_0 \rightarrow S_1$	$\pi_2 \rightarrow \sigma_5$	$n \rightarrow \sigma_g^*$	342.0	0.0000
$S_0 \rightarrow T_2$	$\pi_2 \rightarrow \sigma_6$	$n \rightarrow \sigma_u^*$	335.6	0
$S_0 \rightarrow S_2$	$\pi_1 \rightarrow \sigma_5$	$n \rightarrow \sigma_g^*$	298.8	0.0052
$S_0 \rightarrow S_3$	$\sigma_4 \rightarrow \sigma_5$	$\sigma_u \rightarrow \sigma_g^*$	229.7	0.2832
$S_0 \rightarrow S_4$	$\pi_2 \rightarrow \pi_3$	$n \rightarrow \pi_u^*$	166.1	2.3941
$S_0 \rightarrow S_6$	$\sigma_3 \rightarrow \pi_3$	$\sigma_g \rightarrow \pi_u^*$	144.2	0.4617

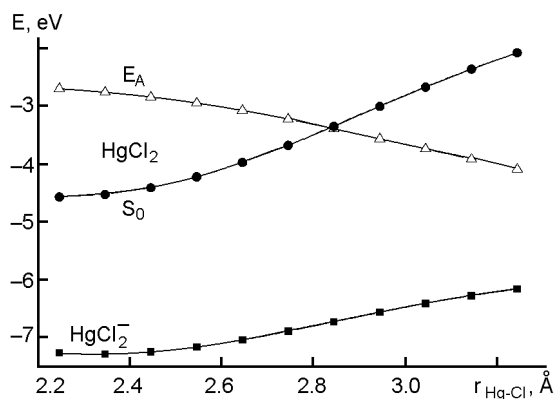


Fig. 3. Potential surfaces of HgCl₂ and HgCl₂⁻ as well as electron affinity energy of HgCl₂ (E_A) as functions of the dissociating Hg–Cl bond length.

Thus, the above-mentioned triplet state is a dissociative one. The direct excitation of the molecule in this fashion will result in dissociation with a high quantum yield. If, however, the excitation is localized at S_1 or T_1 state, the dissociation is possible when the excitation is transferred from those quasi-stationary states on the dissociative T_3 one. It is logical to suppose that the molecule can be excited into all those states only due to generation of primary or secondary ionization electrons having corresponding energy within the sample bulk. A direct absorption of a high-energy quantum cannot result in the molecule excitation into dissociative state.

Since electrons are generated in the sample bulk, those may be captured by mercuric chloride molecule thus forming HgCl₂⁻ anion. The calculations have shown that the anion dissociation in thermalized state is hindered by potential barrier of about 1 eV height (Fig. 3). This barrier is lower than that in mercuric chloride molecule, since the electron affinity energy to the dissociation products is higher than in the molecule (E_A curve in Fig. 3), but it is high enough to freeze the dissociation process. Thus, the radiation-chemical processes are to be expected only proceeding from non-thermalized state. Nevertheless, the dissociation from the anion equilibrium state cannot be excluded totally. The mercuric chloride anion dissociation will result in formation of chlorine anion and a chemically active HgCl particle.

Atoms with two outer electrons are believed to have as a rule a low electron affinity [15] while halogens have maximum affinity values [16]. Thus, the electron affi-

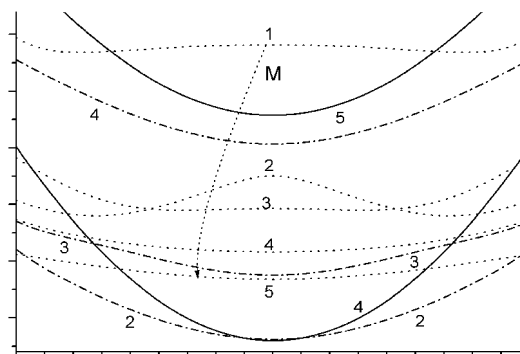


Fig. 4. Potential surface curves for S_0 (solid lines), T ($\pi_2\sigma^*$) (dotted lines) and T ($\sigma\sigma^*$) (dot-and-dash lines) states as functions of Cl–Hg–Cl bond angle at different dissociating Hg–Cl bond length (nm): 0.23 (1), 0.28 (2), 0.3 (3), 0.34 (4), 0.38 (5). M is one of possible paths of dissociation reaction.

ity increase in mercuric chloride molecule with the Hg–Cl bond lengthening can be supposed to be associated with the electron cloud redistribution towards mercury atom, weakening influence of Hg atom and the increased capability of Cl atoms to electron attachment resulting therefrom. In contrast, the ionization energy tends to lowering as the Hg–Cl bond lengthens.

In the dissociation case considered above, the linear molecular structure is retained. In fact, the molecule excitation may cause its sharp bend. In this connection, we have studied the potential surface shapes for the ground state and excited ones of mercuric chloride molecule as functions of the Cl–Hg–Cl bond angle (Fig. 4). It is just the linear molecular configuration that answers to the minimum state energy, as is to be expected for states formed under π -MO involvement. At the same time, the highly excited T ($\sigma\sigma^*$) state energy is maximum for the linear configuration and should decrease as the \angle Cl–Hg–Cl angle diminishes down to 90° . It is just the effect that is observed in the case of equilibrium bond lengths in the molecule ($r = 0.23$ nm). As the dissociating bond lengthens, the T ($\sigma\sigma^*$) state energy decreases while those of all other states, increase (Fig. 2). This results in a stronger configurational interaction between the T ($\sigma\sigma^*$) and other triplet states. Since the corresponding energy levels come together as the molecule becomes bent, the configurational interaction results in a significant repulsion of the states, first of all,

Table 2. Theoretical data for spectroscopic characteristics of Cl-Hg_n-Cl compounds

Molecule	Quantum transition type	Absorption band wavelength, λ, nm		Oscillator strength	
		MNDO/d	AM1	MNDO/d	AM1
Cl-Hg ₂ -Cl	S ₀ → T ₁	442.9	910.8	0.000	0.000
	S ₀ → S ₁	318.9	340.5	0.846	1.061
	S ₀ → S ₂	303.8	332.0	0.004	0.004
Cl-Hg ₃ -Cl (linear)	S ₀ → T ₁	1068.0	709.2	0.000	0.000
	S ₀ → S ₁	461.1	451.0	1.539	2.486
	S ₀ → S ₂	319.5	361.3	0.003	0.003
Cl-Hg ₃ -Cl (kneed)	S ₀ → S ₁	600–110	550–800	0.5–0.2	1.2–0.8
	S ₀ → S ₂	0	410–500	0.06	0.05
	S ₀ → S _n	340–450		0.8–0.1	
Cl-Hg ₄ -Cl (linear)	S ₀ → T ₁	2656	1009	0.000	0.000
	S ₀ → S ₁	605.2	535.9	1.935	4.564
	S ₀ → S _n	209.5		1.132	
Cl-Hg ₄ -Cl (kneed)	S ₀ → S ₁	1026–13	730–780	0.9–0.7	2.1–1.9
	S ₀ → S ₂	00	300–340	1.1–0.9	0.28
		303–338			

in the bent configuration (Fig. 4). As a consequence, the $T(\sigma\sigma^*)$ state energy minimum becomes shifted towards larger $\angle\text{Cl-Hg-Cl}$ angle values. When the $T(\sigma\sigma^*)$ state becomes the lower excited one due to the Hg-Cl bond lengthening, its energy minimum will correspond to the linear molecular configuration.

After the molecule is excited into the $T(\sigma\sigma^*)$ state in the linear configuration, its bending will occur (the molecular symmetry lowering) accompanied by the bond lengthening. The most probable path of dissociation reaction will correspond to the probability distribution of the $T(\sigma\sigma^*)$ state formation as a function of the molecule bending angle as well as to the potential energy gradient at that state surface. As a result, the dissociation reaction path (Fig. 4 shows a version of that path denoted as M) will, at a certain probability, cover the whole potential surface of the $T(\sigma\sigma^*)$ state by a net. Thus, a stronger interaction with lower triplet states will take place for specific paths resulting in the relaxed excitation in those states and a decreased dissociation probability.

In all cases, the reaction product is HgCl having absorption spectra (both its own and its ammonia complex) extending into visible

spectral region but being characterized by very low extinction coefficient. The formed HgCl particle is highly reactive and mobile, thus providing the recombination reactions resulting in mercurous chloride Cl-Hg-Hg-Cl.

Radiation-chemical transformations under short-time irradiation. To interpret experimental data on radiation sensitivity of mercury compound containing films, quantum-chemical studies of mercuric chloride and mercurous chloride were carried out. The radiation-chemical processes involving those compounds must result in formation of active Cl-Hg and Cl-Hg-Hg particles and their recombination products, Cl-Hg-Hg-Hg-Cl and Cl-Hg-Hg-Hg-Hg-Cl. Such molecules are of linear structure typical of sp -hybridization of mercury and chlorine atomic orbitals forming σ bonds. The calculated spectroscopic characteristics of those compounds are presented in Table 2.

Since it follows from experimental data that the film takes a substantial coloration when the irradiated sample is exposed in ammonia vapor, we have carried out calculations for ammonia complexes of the formed molecules, Cl-Hg(NH₃)_n-Cl. In this case, ammonia molecule turns out to be bound with mercury atom under formation of a donor-acceptor bond Hg-N. The presence of such bond results in the $sp \rightarrow sp^2$ re-hy-

Table 3. Theoretical data for spectroscopic characteristics of Cl-(Hg)_m-(NH₃)_n-Cl compounds

Molecule	Quantum transition type	Absorption band wavelength, λ, nm		Oscillator strength	
		MNDO/d	AM1	MNDO/d	AM1
Cl-(HgNH ₃) ₂ -Cl	S ₀ → S ₁	329.9	349.0	0.521	0.953
	S ₀ → S ₂	280.5	262.0	0.162	0.050
Cl-Hg ₃ (NH ₃) ₂ -Cl (linear)	S ₀ → S ₁	454.7	461.2	0.972	2.633
	S ₀ → S _n	236.7	223.6	0.414	0.161
Cl-(HgNH ₃) ₃ -Cl	S ₀ → S ₁	471.7	614.9	0.629	1.067
	S ₀ → S ₂	270.6	349.45	0.115	0.325
	S ₀ → S _n	259.9	303.7	0.291	0.025
Cl-Hg ₄ (NH ₃) ₂ -Cl (linear)	S ₀ → S ₁	625.27	473.0	2.200	6.100
	S ₀ → S _n	238.0	323.5	0.600	0.220
				237.0	
Cl-(HgNH ₃) ₄ -Cl	S ₀ → S ₁	625.4	550.0	0.919	3.176
	S ₀ → S ₂	434.2	466.6	0.002	0.056
	S ₀ → S _n	282.8	374.0	0.562	0.700

bridization of mercury atomic orbitals causing planar structure of the complex with angles between σ bonds close to 120° (in practice, this angle can vary within limits of 120° to 140°). The calculated characteristics of energy structure for the above-mentioned complexes are presented in Table 3.

Comparing the results obtained using both methods, it is seen that in a number of cases the AM1 method gives results close to those obtained using the more accurate MNDO/d. The distinction for some planar (kneel) structures are due to that the geometry of some planar compounds (the configurational interaction being not taken into account) depends significantly on the calculation method.

Since the Cl-Hg_n-Cl molecule in solid solutions is surrounded with fragments of macromolecules and can interact therewith (due to overlapping atomic orbitals of oxygen and mercury), a partial *sp* → *sp*² re-hybridization of mercury AOs is also possible. Therefore, spectroscopic characteristics of corresponding structures have been calculated, too, as is seen in Table 2.

Comparing data from Tables 2 and 3, it is seen that the Cl-Hg₂-Cl complexing with ammonia does not result in coloration. As to Cl-Hg₃-Cl, the matter is somewhat more complicated because the compound must absorb in visible region independent of ammo-

nia presence. The probability of such molecule formation under irradiation of mercuric chloride containing film seems to be rather low, since no appreciable coloration is observed. Cl-Hg₄-Cl molecule is another matter. Its interaction with the environment results in a diffuse band in the red and near IR range, that must cause a weak blue coloration of the material. Interaction with ammonia must result in a strong blackening of the film. Moreover, since Cl-Hg_n-Cl compounds are bound only weakly with ammonia, the complex structure in solid film may have a non-optimal geometry (i.e., the bond angles may be of 120° to 180°). This will cause an absorption band broadening towards shorter wavelengths. As a result, the absorption spectrum of Cl-(HgNH₃)₄-Cl complex will be extended over the whole visible spectral region giving a gray (black) image. A prolonged air exposure of the developed sample results in ammonia evaporation and the visible image disappearance.

Radiation-chemical transformations under prolonged irradiation. Theoretical investigation of films irradiated during long time and exposed in ammonia and water vapors included calculations of geometry and energy structure for Cl-Hg_n-Cl, Cl-(HgNH₃)_n-Cl, Cl-(HgNH₃)_n-Cl·NH₃, and Cl-(HgNH₃)_n-Cl·H₂O molecules.

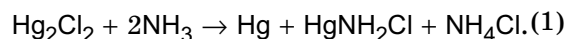
Cl-Hg_n-Cl molecules have been established to be of linear structure. When $n \geq 3$, solutions of those compounds are colored faintly. Interaction between atomic orbitals (AO) of ammonia nitrogen and mercury in Cl-Hg_n-Cl results in a donor-acceptor bond, the ammonia molecule acts as the electron pair donor while mercury atom offers an unoccupied AO. Binding of a mercury atom with three other ones in Cl-(HgNH₃)_n-Cl causes kneeing of linear Cl-Hg_n-Cl molecule and formation of the trans-configuration so that the \angle Cl-Hg-Hg angle is 145° in Cl-(HgNH₃)₂-Cl and 125° in \angle Cl-(HgNH₃)₄-Cl (equilibrium configurations). In the latter case, the \angle Hg-Hg-Hg angle is 120° (104° in AM1) and repulsion of amino groups causes the molecule twisting (about 28° for two Hg-Hg bonds). The complex chain lengthening up to Cl-(HgNH₃)₆-Cl resulted in insignificant changes in the bond angles being 130°, 95°, and 108° along the Cl-(Hg)₆-Cl chain. The twisting angle is 33° in this case.

The donor-acceptor bond turned out to have a low energy being of 0.93 eV in the case of Cl-(HgNH₃)₂-Cl, thus providing a long-term existence of the complex at room temperature (the complex has characteristic lifetime of the order of 10⁴ s, that is, about 3 h, at the frequency factor 10¹² s⁻¹). In Cl-(HgNH₃)₄-Cl molecule, the Hg-N bond energy is 0.74 eV for the 1st and 4th mercury atoms and 0.31 eV for 2nd and 3rd ones. The characteristic dissociation time for the 1st Hg-N bond will be about 10 s while for the 2nd, of the order of one microsecond (the frequency factor can be one decimal order lower for such a weak bond, thus resulting in the characteristic time increase by one order). Thus, the complex containing four ammonia molecules may appear only at a high ammonia concentration under dynamic equilibrium. Similar calculations for Cl-(HgNH₃)₆-Cl give the bond energy 0.7, 0.3 eV and 0.11 eV for the 1st, 2nd and 3rd mercury atoms, respectively. It is clear that under a high ammonia vapor concentration, the 1st mercury atom will be bound with NH₃ permanently, the second one, only under dynamic equilibrium, while the simultaneous binding of all six mercury atoms with ammonia molecules is hardly probable.

Similar studies of mercury atom binding with hydroxyl of the polymer chain have shown that the binding energy of the first mercury atom of Cl-Hg₄-Cl with oxygen is

0.31 eV while that of the second one, only 0.03 eV. Thus, the second mercury atom is essentially never bound with hydroxyl while the first one under dynamic equilibrium is predominantly in the bound state.

Mercuric chloride is known to be capable of the following transformation type in the presence of water and ammonia [5]:



This reaction is irreversible and results in metallic mercury formation. Thus, in mercuric chloride containing films subjected to long-term irradiation, metallic mercury may be released under water and ammonia vapor exposure. It this connection, the potential energy surfaces have been calculated for Cl-(HgNH₃)_n-Cl to clarify if metallic mercury may arise therefrom. The calculated results are shown in Table 4.

The Table presents calculated data for *trans*- (*t*) and *cis* (*c*) Cl-(HgNH₃)_n-Cl complex chains and the reaction products. The bond energy values in *trans*- and *cis*- complexes of mercuric chloride are rather close to one another ($\Delta E = 0.1122$ eV). When no polar medium is present, this fact will result in the *cis*- to *trans*-form ratio of 0.011 at room temperature. Thus, the complex in an apolar medium (e.g., in polymer matrix) is presented mainly by its *trans*-form. This form, however, has a dipole moment close to zero while it attains 12 D for the *cis*-one. The dipole moment of the complex, when interacting with polar solvent, can reduce considerably the energy state of *cis*-form, thus causing a predominance of that form. In our case, no polar solvents were used, therefore, it is the *trans*-form of the complex that exist mainly in the films studied.

The reaction (1) results in formation of rearrangement reaction products:

Table 4. Total bond energy in Cl-(HgNH₃)_n-Cl complexes and in reaction products (calculation by AM1 taking into account configurational interaction)

Complex	Bond energy, eV
<i>t</i> -Cl-(HgNH ₃) ₂ -Cl	29.7201
<i>t</i> -NH ₄ Cl·Hg·NH ₂ HgCl	26.222
<i>c</i> -Cl-(HgNH ₃) ₂ -Cl	29.8323
<i>c</i> -NH ₄ Cl·Hg·NH ₂ HgCl	26.147
<i>t</i> -Cl(HgNH ₃) ₄ Cl	51.881
<i>t</i> -NH ₄ Cl·(HgNH ₃) ₃ ·NH ₂ HgCl	52.589

$t\text{-NH}_4\text{Cl}\cdot\text{Hg}\cdot\text{NH}_2\text{HgCl}$ is formed from $t\text{-Cl-(HgNH}_3)_2\text{-Cl}$ as well as $c\text{-NH}_4\text{Cl}\cdot\text{Hg}\cdot\text{NH}_2\text{HgCl}$ from $c\text{-Cl-(HgNH}_3)_2\text{-Cl}$. This requires an additional energy consumption amounting 3.5 eV for $t\text{-Cl-(HgNH}_3)_2\text{-Cl}$ and 3.69 eV for $c\text{-Cl-(HgNH}_3)_2\text{-Cl}$. Nevertheless, this reaction runs in the presence of water. Thus, the energy loss is compensated due to interaction the resulting dipole moment of reaction products with water molecules. The resulting dipole moment is 12 D for products derived from the *trans*-form and 15 D for those of the *cis*-one. Therefore, the expected interaction will be in fact rather strong, thus explaining the formation possibility of reaction products. In this case, a neutral mercury atom is released and two molecules are formed, namely, NH_2HgCl and NH_4Cl , the latter being dissociated in the presence of water.

The calculation of $t\text{-Cl-(HgNH}_3)_4\text{-Cl}$ molecule and rearrangement reaction product $t\text{-NH}_4\text{Cl}\cdot(\text{HgNH}_3)_3\cdot\text{NH}_2\text{HgCl}$ has shown that in this case, the only energetically favorable hydrogen atom transfer path is the transfer from the fourth ammonia molecule to the second one (or from the first to third one):

The bond energy gain in the formed reaction products is 0.7 eV. It should note that the dipole moment of the initial reagent is nearly zero while that of the reaction products amounts 8.4 D. NH_2HgCl and NH_4Cl molecules are formed due to the reaction as well as three mercury atoms are released. In the reaction products, ammonia molecules are weakly bound with mercury atoms (the highest bond energy does not exceed 0.34 eV), therefore, those are removed rapidly (about 10^{-5} s). Then, the group consisting of three mercury atoms may combine themselves into a rather large light-scattering drop.

We have considered only the initial and final states for the hydrogen transfer reaction in $\text{Cl-(HgNH}_3)_n\text{-Cl}$ complex giving no attention to the reaction coordinate (path). At the same time, hydrogen atom transfer between ammonia molecules bound in the complex is hindered sterically when those molecules are arranged in *trans*-positions to each other. In this case, a long chain of water and/or ammonia molecules should be constructed to simulate the hydrogen transport along that chain. But the longer is such a chain, the lower is the reaction probability. At the same time, hydrogen atom transfer between *cis*-arranged ammonia

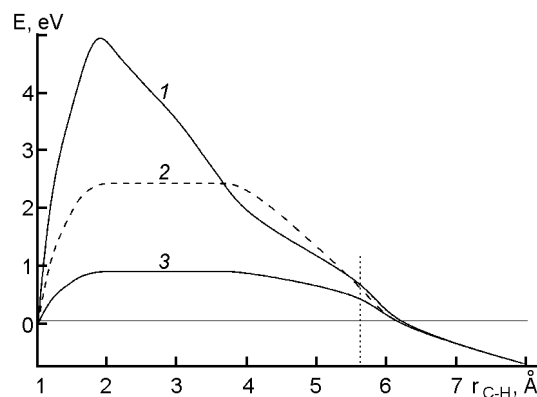


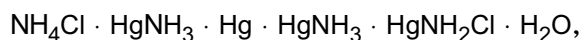
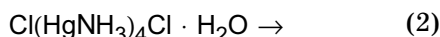
Fig. 5. Energy dependence on the reaction coordinate at transfer of proton ($r < 5.7 \text{ \AA}$) and of NH_4^+ cation ($r > 5.7 \text{ \AA}$) with formation of the reaction final products.

molecules is easy to occur involving only one water molecule (proton transfer from ammonia to water followed by its transfer to the second ammonia molecule). Thus, it is just the water-catalyzed proton transfer in the *cis*-form of mercuric chloride/ammonia complex that is the most probable mechanism of the reaction (1). In turn, the *cis*-complex is formed only in the presence of a polar solvent (in the experiment, mercuric chloride powder in ammonia water was used [5]).

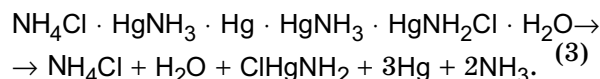
The matter is much better with $t\text{-Cl-(HgNH}_3)_4\text{-Cl}$ complex containing two neighboring ammonia molecules. The proton transfer between those turned out to be of energy favor in non-polar solid solvent (polymer matrix). There is a high potential barrier against the proton transfer in that complex (ammonia molecules approaching due to vibration process was not taken into account in calculations). This barrier can be lowered using a catalyst. To check the model, the calculation was carried out for only one ammonia or water molecule. The calculated results are shown in Fig. 5. The barrier height exceeds 5 eV in the absence of catalyst while the presence of one ammonia molecule causes the barrier lowering down to 2.4 eV and water, to 0.9 eV. The account for vibrations of the complex components may result of course in some reduction of the values found. Thus, the reaction is possible only if water is present. The simultaneous involvement of several ammonia and water molecules seems to favor the further lowering of the energy barrier.

Thus, the main process causing appearance of a stable image in irradiated polymer films containing mercuric chloride is proton

transfer reaction in $t\text{-Cl}-(\text{HgNH}_3)_4\text{-Cl}$ complex running in the presence of water (or water and ammonia) vapors:



this hydrogen atom transfer reaction offers the energy gain of 0.7 eV. Then the formed complex is decomposed at a sufficiently high (e.g., room) temperature due to its instability:



Thus, irradiation of polyvinyl alcohol films containing mercuric chloride with high-energy quantum (about 3 keV) followed by exposure in ammonia vapor results in appearance of image. The X-ray sensitivity of the materials is due to ionization and dissociation of HgCl₂. Formation of Hg₄(NH₃)₄Cl₂·H₂O complex in a sufficient concentration and the image formation requires about 20 min irradiation time (in the specified experiment conditions) to attain the critical concentration of Hg atoms in the film that is defined by the necessity of mercury microdrop formation. These microdrops scatter the light, thus causing imaging effect of vesicular type.

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Матеріали на основі HgCl₂ для реєстрації рентгенівського випромінювання

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Виконано дослідження плівок полівінілової спирт/сулема HgCl₂, які включають квантово-хімічні розрахунки енергетичної структури, потенціальної поверхні основного, збудженого та іонізованого станів сулеми, а також продуктів розкладу сулеми з аміаком. Опромінення шарів високоенергетичними квантами радіації (~3 кеВ) з наступним витриманням у парі аміаку приводить до появи зображення. Показано, що найбільш імовірним механізмом радіаційно-хімічних процесів є збудження молекули сулеми вторинними електронами у дисоціативний стан з наступною дисоціацією. Оптичний контраст досягається внаслідок утворення у плівці комплексу Hg₄(NH₃)₄Cl₂·H₂O та конденсації в умовах опромінення мікрокрапель ртуті, що розсіюють світло та спричиняють ефект зображення типу везикулярного.