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Physicochemical Properties and Laser Initiation of a Copper Perchlorate Complex with 3(5)-Hydrazino-4-amino-1,2,4-triazole (HATr) as a Ligand

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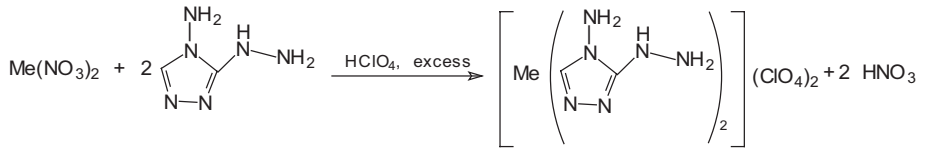
Abstract: Several metal perchlorate complexes with 3(5)-hydrazino-4-amino-1,2,4-triazole as a ligand were investigated. It was shown that the threshold of laser initiation of the copper complex changed under the influence of additives of optically transparent polymers, detonation nanodiamonds or nanotubes.

Keywords: IR-laser, pulse, ignition, complex perchlorates of metals, 3(5)-hydrazino-4-amino-1,2,4-triazole (HATr) as a ligand, light-sensitive explosives

Introduction

Copper and some other d-metal perchlorate complexes with 3(5)-hydrazino-4-amino-1,2,4-triazole (HATr) as potential light-sensitive explosives were synthesized several years ago in the Saint-Petersburg State Institute of Technology [1]. Heterocyclic ligands with a high positive enthalpy of formation are easily oxidized by central and perchlorate ions. The first steps of the decomposition mechanism and the central ion effect on the sensitivity of the metal complexes to a laser mono pulse (λ = 1064 nm, τ = 30 ns, d = 0.48 mm) were thoroughly investigated for these complexes as potential photosensitive, energetic, coordination compounds. The preparative procedures for the complex salts are described in article [2]:



where Me = Cu^{2+}(**1**), Cd^{2+}(**2**), Ni^{2+}(**3**), Co^{2+}(**4**).

The reactions were performed at room temperature in dilute $HClO_4$. A solution of 0.01 mol of metal nitrate **1-4** in 10 cm^3 of propan-2-ol was added to a solution of 0.02 mol of HATr in a mixture of 10 cm^3 of propan-2-ol and 5 cm^3 of ~ 60% $HClO_4$. The reaction mixture was stirred for 1 h. The precipitate of the metal complex **1-4** was filtered off, washed with water, propan-2-ol and dried at 50 °C in vacuum. The composition and structure of the metal complexes **1-4** were supported by the results of elemental analysis and IR spectroscopy. Coordination compounds **1-4** detonate under laser pulse irradiation (Table 1).

Table 1. Laser initiation of metal complexes **1-4**

Complex	Effect	Minimal energy W_{min}, J	Ionization potentials of metals I_1+I_2, eV [3]
$[Cu(HATr)_2](ClO_4)_2$ (**1**)	detonation	$1.1\cdot10^{-5}$	28.02
$[Cd(HATr)_2](ClO_4)_2$ (**2**)	detonation	$5.03\cdot10^{-4}$	25.90
$[Ni(HATr)_2](ClO_4)_2$ (**3**)	detonation	$5.75\cdot10^{-4}$	25.78
$[Co(HATr)_2](ClO_4)_2$ (**4**)	detonation	$1.36\cdot10^{-3}$	24.92

W_{min} – minimal energy of the laser beam for initiation of detonation of a metal complex.

It was concluded on the basis of the experimental results that the sensitivity of compounds **1-4** to a laser mono pulse is correlated with the oxidizing ability of the central metal ion (expressed as the sum of two ionization potentials, I_1+I_2). The greater this value is, the higher is the sensitivity of the compound towards laser radiation:

$$\mathbf{Cu > Cd > Ni > Co}$$

The fact that the inner sphere ligand oxidation was effected by the metal ion proved that the reaction of the ligand with a metal ion is the first step of the initiation process. The results of the investigation allow us to assume that initially the following mechanism of oxidation takes place:

$$\mathbf{2\ ClO_4^- + Me^{2+} \rightarrow ClO_4^{\bullet} + Me^{+} + ClO_4^-}$$
$$\mathbf{ClO_4^- + Me^{+} \rightarrow ClO_4^{\bullet} + Me^{\circ}}$$

The two-step interaction of the metal cation and the perchlorate anion results in the formation of a highly active perchlorate free radical participating in the second step of ligand oxidation **[**2**]**.

Salts **1-4** have a short deflagration-to-detonation transition (DDT) distance. For example, a minimum initiating charge of copper complex **1** for the pressed charge of RDX in the detonating cap No. 8 is equal to ~ 0.025-0.030 g. Unfortunately, the salts **1-4** so prepared are rather hazardous explosives, because they have high sensitivity to mechanical stimuli, similar to that of industrial primary explosives such as lead azide or lead styphnate [4].

Properties of copper perchlorate complex 1

Copper perchlorate complex **1** has been carefully studied as the most effective light-sensitive compound among the investigated metal complexes of 3(5)-hydrazino-4-amino-1,2,4-triazole as a ligand. Optimization of the laboratory procedure for complex **1** preparation was the first step in our work. The protocol for copper complex **1** synthesis was published in [5]. We improved this method and subsequently used it for the preparation of complex **1**.

An aqueous solution of copper(II) perchlorate (4 cm^3) with the salt concentration 1.088 $mol \cdot l^{-1}$ (0.043 mol) was added to a mixture of 3.12 g (0.013 mol) of HATr and 3.04 g (0.026 mol) of NH_4ClO_4 in 24 cm^3 of water at ~17 °C. The reaction mixture was then stirred for ~3 h at the same temperature. Subsequently 1.7 cm^3 of ~60% $HClO_4$ was added to the reaction mass and the mixture was stirred for an additional 2 h. After adding ethanol (13 cm^3) the mixture was stirred for a further 2 h. The green precipitate of copper(II) perchlorate complex **1** was filtered off, washed with cold water, with ethanol and dried for 3 h at 30 °C under vacuum. Copper complex **1** (1.62 g, 75% yield) was isolated.

The IR spectrum of complex **1** exhibited no bands for the NO_3^- ion. This implies the complete exchange of anion NO_3^- for ion ClO_4^- in the outer sphere of complex **1**. The bands of ClO_4^- in complex **1** were identical to the bands of the ClO_4^- anion in simple perchlorates. That demonstrated that the anion ClO_4^- did not coordinate with the central copper ion.

The electronic absorption spectrum of 0.02 $mol \cdot l^{-1}$ aqueous solution of complex **1** was recorded on a spectrometer Shimadzu UV 2401 (Japan) (Figure 1).

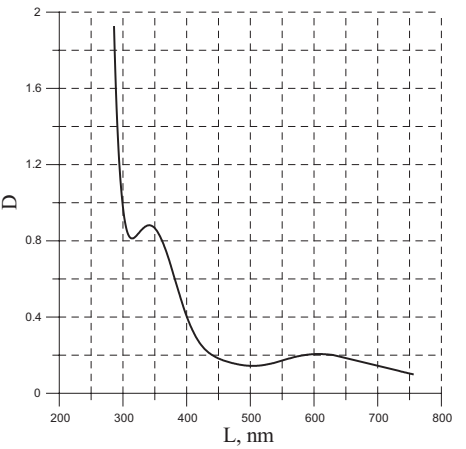


Figure 1. The absorption spectrum of an aqueous solution of copper complex **1**.

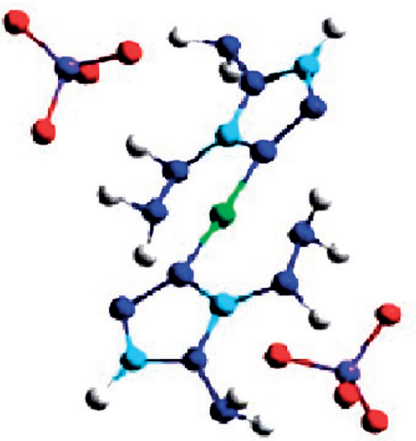


Figure 2. Molecular complex [bis-3(5)-hydrazino-4-amino-1,2,4-triazole] copper(II) perchlorate.

As can be seen in Figure 1, the absorption maximum of complex **1** lies at a wavelength shorter than 300 nm, being close to the absorption area of the ligand. The absorption spectrum of perchlorate complex **1** in the region of the d-d transition has two bands: near 340 nm and ~600 nm. Hence the octahedral structure of copper complex **1** may be suggested [6]. An aqueous solution of complex **1** has a weak absorption in the IR region (longer than 800 nm). Consequently, aqueous solutions of copper perchlorate complex **1** at the wavelength of Nd-laser irradiation (λ=1064 nm) have weak extinction coefficients.

The structure of copper perchlorate complex **1** in the gaseous phase was calculated by quantum-chemical methods. Calculations were performed with the use of the specialized quantum-chemical Gaussian 98 program set [7]. The semi-empirical PM3 method was used for the initial optimization of molecular complex **1** structures. The DFT method was utilized using the B3LYP functional. The preliminary calculations for copper complex **1** were carried out with the use of the split valence 3-21G basis set. The final calculations were carried out with the use of the polarized 6-31G(d) basis set. The optimized structure of molecular complex **1** is shown in Figure 2. It should be noted that the structure obtained for the free molecular complex **1**, treated as a molecule in the gaseous state, can be different from its structure in the crystal lattice.

The thermal decomposition of molecular metal complex **1** starts with the transfer of a proton from the ligand to the perchlorate anion with the formation of molecular $HClO_4$. The $HClO_4$ so formed is an effective oxidizer participating in further redox processes. The calculated value of the bond dissociation energy for proton transfer is equal to 136.1 kJ/mol. This value is lower than the value of the complex **1** dissociation energy for the formation of free ClO_4^- ions (346.4 kJ/mol).

Comparison of the initial steps of decomposition of complex **1** in the crystal and gaseous states shows that the mechanism of dissociation depends on the state of aggregation of the coordination compounds [2, 7].

The size of crystals of complex **1** was estimated with a scanning electron microscope JSM-35CF (JEOL). The results of this investigation for copper complex **1** are shown in Figures 3-5 and Table 2.

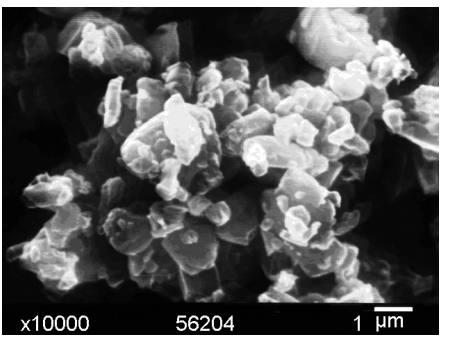


Figure 3. SEM image of copper complex **1** (sample 1), magnified ×10000.

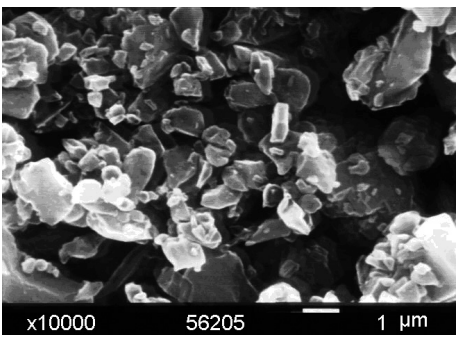


Figure 4. SEM image of copper complex **1** (sample 2), magnified ×10000.

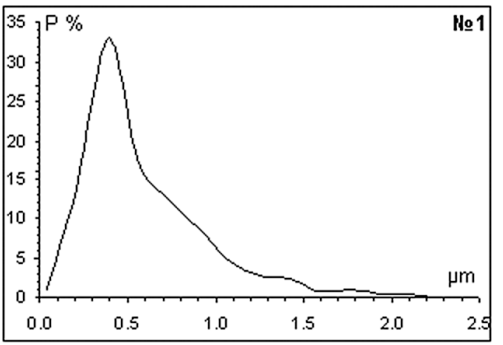


Figure 5. Histogram of complex **1** particle size distribution.

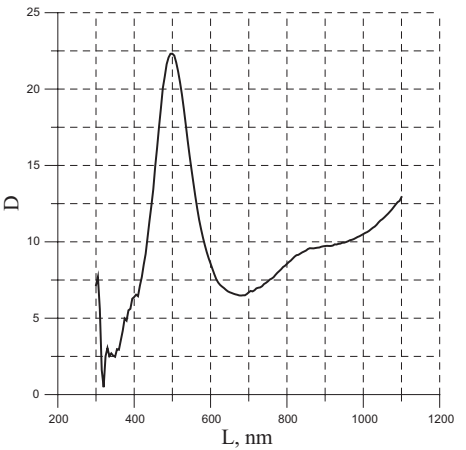


Figure 6. Spectrum of surface reflection of the light-sensitive composite EC-1.

Table 2. Size of complex **1** particles

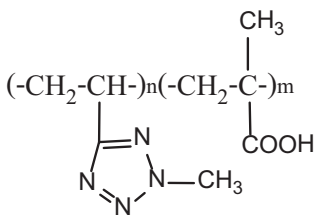
No.	N	d_{min}-d_{max}	d_{mean}	K_f
1	764	0.04-2.47	0.53 ± 0.32	0.81

N stands for the quantity of particles in the data file used for calculation, d_{mean} – for the mean diameter of particles.
($d_{mean} = (d_{min} + d_{max})/2$, where d_{max} and d_{min} are the maximum and minimum sizes of the sample particles, K_f characterizes the particle form.

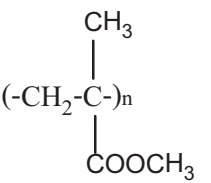
As can be seen in Figures 3-5 and Table 2, copper complex **1** is an ultradispersed material with the mean size of crystals ~0.5 μm. The particle surface form was calculated from equation $K_f = 4\pi S/P^2$, where S – particle

area, P – perimeter of the particle. The calculated value of K_f is equal to 0.81. Consequently, the particles of copper perchlorate complex **1** have irregular surface form.

As was mentioned earlier, the sensitivity of salt **1** to mechanical stimuli is the same as in the case of industrial primary explosives (lead azide or lead styphnate). Such a high level of danger for copper complex **1** makes its practical use as a light-sensitive energetic material very problematic. Minimizing the level of danger of perchlorate complex **1** may be achieved by mixing it with an optically transparent polymer. Addition of 10-20% of polymer decreases the sensitivity of the light-sensitive composite to mechanical stimuli to the level of danger of regular organic HE, for example, pentaerythritol tetranitrate (PETN) or hexanitrohexaazaisowurtzitane (CL-20). These light-sensitive composites are relatively safe during handling, storage and transportation. In this work two optically transparent polymers were tested: energetic co-polymer of 5-vinyl-2-methyltetrazole (98%) and methacrylic acid (2%) (polymer PVMT) or inert poly(methyl methacrylate) (organic glass, Plexiglas, PMMA).



PVMT



PMMA

Samples prepared from a polymer bound copper complex **1** may have different spectra for light absorption in the visible and IR ranges as compared with the aqueous solutions of the copper complex. This hypothesis was experimentally tested. The electron reflection spectrum of the film prepared from a mixture of 90% complex **1** and 10% of polymer PVMT (composite EC-1) was recorded using spectrometer Specord 200M (Carl Zeiss, Germany) (Figure 6). The surface of the composite EC-1 film has minimum reflection (or maximum absorption) in the UV range at wavelengths shorter than 350 nm. The surface of the sample has maximum reflection in the range of wavelengths 400-600 nm (visible light), with reflection extremum near 500 nm. The aqueous solution of perchlorate complex **1** has minimum optical density also near 500 nm (Figure 1). Reflection of the surface of the film sample increases at longer wavelengths (IR range). But the absolute gradient of this inversion is lower than that in the visible range.

Initiation of the polymer bound composites of copper complex 1 by a Q-switch Nd-laser pulse

Initiation of light-sensitive explosives by a laser pulse has special features in comparison with the alternative methods of initiation.

It was found that the thresholds of initiation of film charges of composite EC-1 by a Q-switch laser pulse (mono pulse) ($\lambda = 1.06$ μm, $\tau = 30$ ns) depended on their thickness. The thickness of film charges was calculated as the mass of the explosive per unit area of the charge (as mg/cm^2). The thresholds of initiation of composite EC-1 increase when the thickness of the film charges becomes lower than $m_s = 60\text{-}70$mg/cm^2 (Figure 7). Film charges having a thickness less than $m_s = 20$ mg/cm^2 were impossible to initiate by a Q-switch laser beam even when the energy density was 15 times higher than the threshold of initiation of ~1 mm samples.

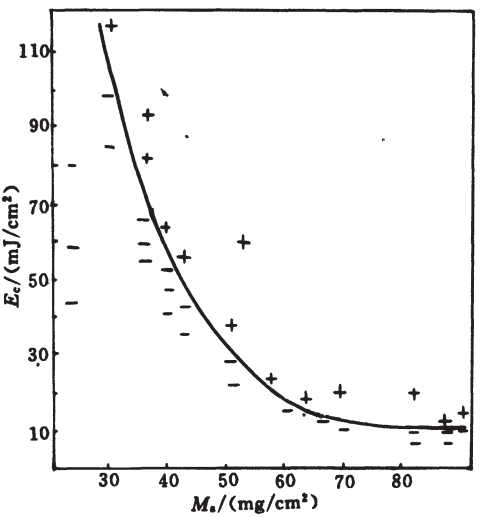


Figure 7. Dependence of the critical density of laser energy of initiation (E_c) on the specific mass (M_s) of light-sensitive film charge EC-1. (Diameter of laser beam is equal to 4.7 mm)
"+" – explosion; "–" – failure

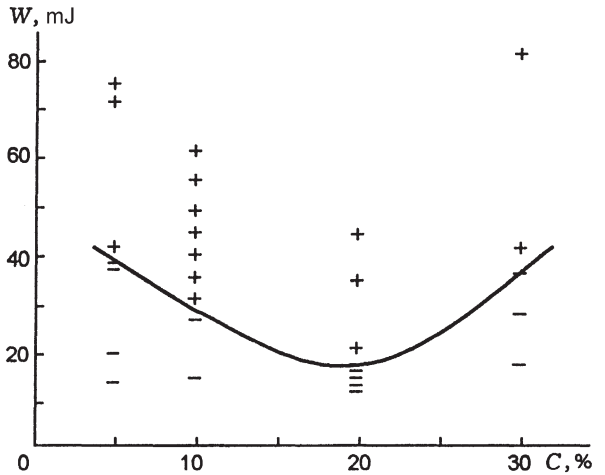


Figure 8. Dependence of the threshold of initiation of film charges of copper complex **1** on the concentration of PMMA as a polymer matrix. (Diameter of laser beam is equal to 2.8 mm)
"+" – explosion; "–" – failure

As can be seen in Figure 7, the threshold of initiation of composite EC-1 becomes constant if the thickness of the film charges exceeds 70-80 mg/cm^2 (~0.8-0.9 mm). So, further investigations were aimed at finding a correlation between the thresholds of laser pulse initiation and the concentration of polymer in light-sensitive film charges, as well as a correlation between the time of delay of ignition of samples and the density of energy of the laser beam. The data were plotted for film charges with thickness 2-3 mm. In these experiments PMMA polymer was used as a matrix for light-sensitive composites. The investigations were performed using the setup described in [8]. The duration of the laser pulse was equal to ~10.1 ns.

The influence of the polymer content on the sensitivity of the film charges of light-sensitive composites to pulse laser irradiation is a real problem. The polymer as an inert additive must decrease the sensitivity of the copper complex **1** to the laser Q-switch pulse. But the PMMA polymer is optically transparent to laser irradiation. So, the presence of the polymer matrix must increase the volume of absorption of laser energy; conditions of hot spots formation are enhanced and thresholds of initiation are decreased. The experimental dependence of the initiation thresholds of film charges of the composite based on the PMMA polymer containing copper complex **1** is given in Figure 8. Increasing the PMMA concentration up to ~20% causes a decrease in the threshold energy of initiation

for film charges. Apparently, this is a result of increasing the light transparency of the film charges of energetic composites with increasing polymer concentration, the conditions of hot spot formation becoming more favorable. The increase of the initiation threshold of energetic film charges with increased PMMA concentration beyond ~20% is probably the result of decreasing the specific explosion energy of the composite including an inert additive.

Times of delay of initiation of light-sensitive compounds and composites often determine the area of their practical use. Experimental dependences of times of ignition delay on the density of laser energy for the samples of film charges of a light-sensitive composite containing copper complex **1** and PMMA (concentration of polymer being 15% and 20%, correspondingly) are given in Figure 9.

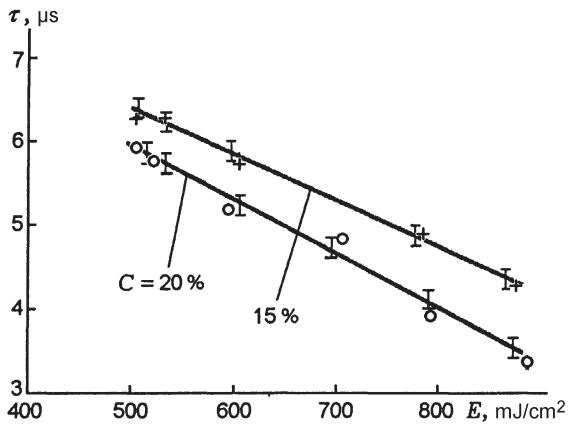


Figure 9. Dependence of the time of ignition delay on the density of laser energy for samples of film charges of light-sensitive composites containing copper complex **1** and PMMA.

It should be noted that the time of ignition delay for the charges containing 15% of the polymer is higher compared to that of the samples containing 20% of PMMA.

At first glance the situation should be quite the opposite. The higher the content of metal complex **1** in the composite is, the shorter should be the time of flaming up of the samples. But this is not the case.

Probably the time of generation of the ignition source is determined mainly by the time for hot spot formation, whereas the time of deflagration-to-detonation transition comprises a relatively minor part of the total observed time of the ignition delay.

The plots shown in Figures 8 and 9 contradict the hypothesis of a thermal mechanism of ignition of light-sensitive copper complex **1** resulting from heating of the optical micro heterogeneities of the species.

The experimental data presented in Figure 7 suggest that the ignition of light-sensitive film composites based on complex **1** by short laser mono pulses depends, to a considerable degree, on the unloading of the material by the rarefaction waves.

The influence of additives on the sensitivity of copper complex 1 to a free generation Nd-laser pulse

The free generation laser pulse is another form of laser irradiation for initiation of light-sensitive energetic materials. The free generation laser pulse (single pulse) consists of a series of pulses that are repeated within ~10^{-6} s. The full duration of a single pulse lasts several milliseconds.

The threshold of initiation of pressed charges of copper complex **1** and composite EC-1 by the free generation laser pulse of a Nd-laser Model IT-181 (Russia) were measured. The charges of the investigated explosives were pressed under 60 MPa in copper caps of 5×2 mm size. The Nd-laser Model IT-181 had the following irradiation parameters : $\lambda = 1.06$ μm, $\tau_q = 2$ ms, the energy of the laser pulse varied within the range 10-4000 mJ, the diameter of the laser beam was equal to 1 mm. The scheme of the experimental setup is shown in Figure 10.

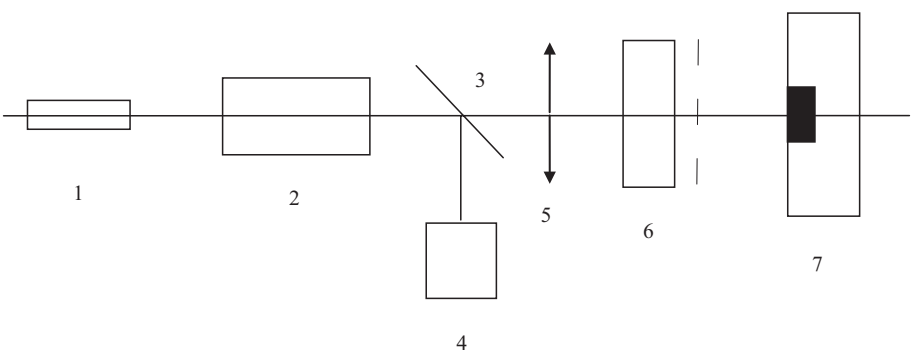


Figure 10. Schematic drawing of the experimental laser setup. 1 – He-Ne testing laser ($\lambda = 0.62$ μm), 2 – experimental laser IT-181, 3 – laser beam splitter plate, 4 – gauge of laser power irradiation IMO-2N (Russia), 5 – lens, 6 – neutral light filters, 7 – cassette with the sample of a film charge of the light-sensitive composite.

The laser beam illuminated the central part of the charge. The size of the illuminated zone was adjusted by moving the lens (5). A gauge of laser power irradiation IMO-2N (4) was applied to control the energy of the laser beam under reflected irradiation from the light splitter plate (3). A neutral light filter (6) was used for additional attenuation of laser irradiation. He-Ne laser (1) was applied for testing the optical scheme of the laser setup.

The first part of the investigation consisted in studying the influence of addition of an optically transparent polymer on the threshold of initiation of copper complex **1**. The results of the experimental determination of the initiation threshold of copper complex **1** and of composite EC-1 are shown in Table 3.

Table 3. Results of laser initiation of copper complex **1** and composite EC-1

Sample	Pressed charge of copper complex **1**	Pressed charge of composite EC-1
Threshold of laser initiation (the energy density, E, J/mm^2)	0.44	0.135

The presented values are mean values from six parallel experiments. The average uncertainties of experiments are equal to 10%.

The results in Table 3 show that composite EC-1 has a threshold of laser initiation about one third that of copper complex **1**. Comparison of the data from Table 3 and Figure 8 demonstrated that the addition of an optically transparent polymer to copper complex **1** in concentrations up to ~20% decreased the threshold of Nd-laser pulse initiation both to mono- and single pulses. Such a comparison also showed that the threshold of laser initiation of composite EC-1 by a free generation pulse is approximately 100 times higher than the threshold of laser initiation by Q-switch laser pulse. Such a result was expected, because a part of the irradiation energy is lost in the case of the single pulse.

The ultra disperse soot (carbon black) is known to be used for decreasing the threshold of initiation of light-sensitive energetic metal complexes by laser diodes and mono pulse generation lasers [9]. But the influence of the addition of other allotropic forms of carbon to light-sensitive energetic metal complexes on their threshold of initiation by a single laser pulse is unknown.

So the next step of the investigation was to determine the influence of addition of detonation nanodiamonds (DND, fraction 40-60 nm, produced by "Diamond's Center", Saint-Petersburg) and multiwall nanotubes (NT, size <100 nm, produced by "Astrin", Saint-Petersburg) on the threshold of laser initiation of composite EC-1. In these experiments a free generation pulse Nd-laser Model IT-181 was used. DND or NT (3 mass%) was added to a suspension of copper complex **1** in a solution of polymer PVMT in a volatile organic solvent or to

a suspension of composite EC-1 in the same solvent. After careful mixing of the suspensions for ~15 minutes and evaporation of the solvent, 2 mm thick films of light sensitive composites were prepared. In the specimens so prepared submicron particles of copper complex **1** and nanosized species of carbon additives were uniformly distributed in the polymer matrix. The central part of the charges was illuminated by the laser beam (Figure 10). Some of the experimental results of the laser initiation threshold determination of light-sensitive composites are given in Table 4.

Table 4. Results of laser initiation of film charges of light-sensitive composites

Sample	Film charge of composite EC-1 + 3% DND	Film charge of copper complex **1** + 3% DND + 10% PVMT	Film charge of copper complex **1** + 3% NT + 10% PVMT
Threshold of laser initiation (energy density, E, J/mm^2)	0.06	0.034	0.051

The values shown are mean values from six parallel experiments. The average uncertainties of experiments are equal to 10%.

Sometimes deflagration of the composite took place instead of detonation below the critical energy of the laser beam for copper complex **1** + 3% DND + 10% PVMT. Similarly, the deflagration of composite EC-1 at the critical energy of the laser beam also took place.

Comparison of the results shown in Tables 3 and 4 allows the following conclusions:

- Addition of DND or NT in the amount of 3% decreases the threshold of laser initiation of composite EC-1 3-4 -fold,
- The effect of DND as a sensitizing additive depends on the method of preparation of the light-sensitive composite,
- The effect of sensitization by DND is stronger than the effect of NT if the composites are prepared using the same method.

Conclusions

The sensitization effects of additives of optically transparent polymers, detonation nanodiamonds and multiwall nanotubes on laser initiation of bis-(3(5)-hydrazino-4-amino-1,2,4-triazole)copper(II) perchlorate are experimentally demonstrated.

Acknowledgments

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