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Laser Initiation of Complex Perchlorates of *d*-Metals With Heterocyclic Ligands

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Abstract: Several *d*-metal perchlorate complexes with 3-hydrazino-4-amino-5-R-1,2,4-triazoles as ligands (where R = H, CH_3, SH) were investigated. It was shown that SH-group inhibited radical processes of thermal decomposition and burning of the complexes and also increased the thresholds of their Q-switch IR-laser initiation compared with the salts where as R = H, CH_3-groups decreased the sensitivity of the metal complexes to laser initiation.

Key words: physical chemistry; IR-laser; pulse; ignition; complex perchlorates of *d*-metals; 3-hydrazino-4-amino-5-R-1,2,4-triazoles ligands; light-sensitive explosives.

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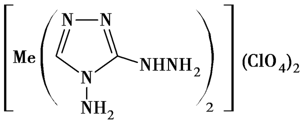
1 Introduction

Nowadays the electrical way of blast-caps initiation is traditional. But the devices used for this process are inherently susceptible to an accident initiation by external stimuli such as an electrostatic discharge (ESD), electromagnetic interference (EMI), and radio wave irradiation (RI). Pulse laser initiation of explosives is a new perspective method. Pulse lasers provide practical means of electrical isolation of the energetic materials, thereby eliminating hazards associated with ESD, EMI and RI[1,2]. Coordination perchlorate complexes of transient metals represent an interesting and perspective class of explosives for laser detonators[3].

2 Laser Initiation of Perchlorates of Transition Metal Complexes With 3-Hydrazino-4-amino-5-R-1,2,4-Triazole as Ligand

Several years ago in the Saint-Petersburg State Institute of Technology some perchlorate complexes of *d*-metals with 3(5)-hydrazino-4-amino-1,2,4-triazole as potential light-sensitive explosives were synthesized[4]. The heterocyclic ligand has high positive enthalpy of formation and can be easily oxidized by the central and perchlorate ions. In search for new photosensitive energetic coordination compounds and for the study of the central ion effect on the sensitivity of metal complexes to laser mono pulse ($\lambda = 1060$ nm, $\tau = 30$ ns), complex perchlorates of copper (II) (**1**), cobalt (II) (**2**), nickel (II) (**3**) and cadmium (II) (**4**) (see in Scheme 1) with this ligand were prepared and investigated. The prepared salts have the general formula given below, where Me = Cu^{2+} (**1**), Cd^{2+} (**2**), Ni^{2+} (**3**), Co^{2+} (**4**)



Scheme 1

Coordination compounds **1 – 4** detonate under laser pulse irradiation. On the basis of the results of testing it was concluded that the sensitivity of compounds (**1 – 4**) to laser mono pulse 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, the higher is the sensitivity of the compound towards laser radiation[5]:

$$Cu > Cd > Ni > Co$$

The inner sphere ligand oxidation effected by the metal ion was proved to predominantly occur at the initial stages of the initiation process. The results of the study allow to assume that at the initial stages the following mechanism of oxidation takes place:

$$2ClO_4^- + Me^{2+} \longrightarrow ClO_4^{\cdot} + Me^+ + ClO_4^-$$

$$ClO_4^- + Me^+ \longrightarrow ClO_4^{\cdot} + Me^{\circ}$$

The two-stage interaction of the metal cation and the perchlorate anion results in the formation of a highly

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active perchlorate radical participating in the second stage of ligand oxidation[6].

Salts **1 – 4** have a short deflagration-to-detonation (DDT) distance. For example, a minimum initiating charge of copper complex **1** for the pressed charge of secondary explosive, RDX, in the blast cup No 8 equals to ~0.025 – 0.030 g. Unfortunately, the so prepared salts **1 – 4** are very hazardous explosives, they have high sensitivity to mechanical stimuli approaching the sensitivity of industrial primary explosives[3,7]. The thresholds of initiation of PBX charges of complex **1** depend on their thickness (see Fig. 1)[7].

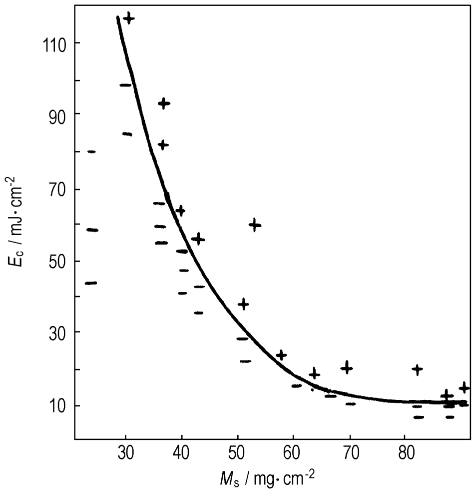
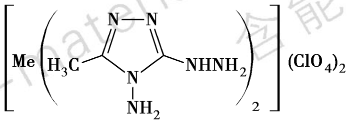


Fig. 1 Relationship between critical initiation energy (E_c) and the mass of complex **1** explosive formulation (M_s) (laser beam diameter 4.7 mm ; 10% of polymer)

The time of the ignition delay of PBX charges of complex **1** under Q-switch laser irradiation (λ = 1.064 μm, τ_q = 10.1 ns) decreased from ~6.5 μs to ~3.2 μs when the energy of laser beam became about twice as much as the threshold of initiation[8]. It is of theoretical and practical interest to study the influence of substituents in position 5 of 3(5)-hydrazino-4-amino-1,2,4-triazole upon the laser sensitivity of corresponding *d*-metal complex perchlorates.

The coordination perchlorate complexes of Hg^{2+}, Cu^{2+} and Co^{2+} with 3-hydrazino-4-amino-5-methyl-1,2,4-triazole were shown to have lower sensitivity to impact compared to the corresponding complex salts of 3(5)-hydrazino-4-amino-1, 2, 4-triazole[9]. The structure of perchlorates of transition metal complexes with 3-hydrazino-4-amino-5-methyl-1,2,4-triazole as ligand, where Me = Hg^{2+}, Cu^{2+}, Co^{2+} (see in Scheme 2).



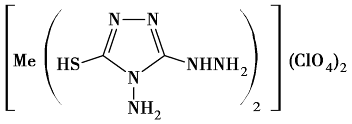
Scheme 2

Unfortunately, these salts only burned but did not explode or detonate under beam pulses of neodymium Q-switch glass laser[10]. This feature excludes the application of coordination salts with 3-hydrazino-4-amino-5-methyl-1,2,4-triazole as ligand in optical blast cups[1,3].

3-Hydrazino-4-amino-5-mercapto-1,2,4-triazole (trade mark "Purpald") was the next investigated ligand in light-sensitive complex perchlorates of *d*-metals. The SH-group imparts the properties of radical trap to the ligand.

So this ligand can inhibit radical chain reactions by trapping, for example, OH˙, RO˙, ROO˙ radicals. Since burning and decomposition of complex perchlorates under mechanical stimuli are radical chain processes, Purpald perchlorate complexes are expected to be less sensitive to thermal stimuli and show lower inflammation ability in comparison with perchlorate complexes of *d*-metals with 3(5)-hydrazino-4-amino-1,2,4-triazole as ligand.

The precocious mechanisms of laser pulse initiation of coordination perchlorate complexes of *d*-metals with substituted 1, 2, 4-triazole as ligands are unknown[3,8]. That is why the level of sensitivity of perchlorate complexes of *d*-metals with Purpald as ligand to pulse irradiation of the neodymium laser cannot be suggested a priori. For the experimental verification of our hypothesis the perchlorate complexes of copper (II), cadmium (II), nickel (II) and cobalt (II) with Purpald as ligand were synthesized (see in Scheme 3), where Me = Cu^{2+} (**5**), Cd^{2+} (**6**), Ni^{2+} (**7**), Co^{2+} (**8**)



Scheme 3

In order to study the details of the mechanism of laser pulse initiation and to evaluate the level of sensitivity of these complex salts, charges of complex perchlorates **5 – 8** were pressed in copper caps forming the layer ~1.5 mm thick with 5 mm diameter. Two pulse lasers were used in our experiments, a Q-switch neodymium glass laser with the time of pulse ~30 ns, and a free generation mode neodymium containing potassium-gadolinium tungstate crystal laser, with the time of pulse ~100 μs. The energy of laser beam irradiation was corrected by optic glass filters and was recorded as reported in the literature [3,7]. The central part of the charge was illuminated with the laser beam. The results of experiments on laser initiation of perchlorate complexes **5 – 8** are presented in Table 1.

Table 1　Laser initiation of perchlorate complexes 5 – 8 by free generation mode pulse

($\lambda = 1{,}06$ μm, $\tau_q = 100$ μs, $d_{beam} = 1$ mm, $E = 0{,}2$ J)

complex	effect
$Cu(C_2H_5N_6S)_2(ClO_4)_2$	explosion
$Cd(C_2H_5N_6S)_2(ClO_4)_2$	explosion
$Co(C_2H_5N_6S)_2(ClO_4)_2$	explosion
$Ni(C_2H_5N_6S)_2(ClO_4)_2$	explosion

The performed experiments with free generation mode laser irradiation show that all of the investigated complexes are light sensitive compounds. The preliminary experiments with Q-switch laser irradiation have shown the copper perchlorate complex **5** to have the lowest threshold of initiation among the investigated perchlorate complexes **5 – 8**, but only charges of compound **5** could be exploded in the experiments (see in Table 3). This result did not agree with that reported in ref. [11]. The authors of this work could not ignite copper complex **5** by irradiation of a Q-switch laser. Supposedly, the Polish researches had a Q-switch laser with the power insufficient to explode the copper perchlorate complex **5**.

The performed experiments have also shown that copper perchlorate complex **5** had sensitivity to impact equal to 36% (drop-hammer K-44-2, a standard procedure according to GOST 4545-88, apparatus No 1, height 25 cm, hammer mass 2 kg). Pentaeritritol tetranitrate (PETN) had sensitivity to impact 12% under the same conditions. In compliance with our experimentations, the copper perchlorate complex **5** turned out to be more safe than other primary explosives, for example, the copper perchlorate complex **1**. So the safety of compound **5** was near the level of safety of modern high explosives[9], for example, PETN, CL-20, etc.

The copper perchlorate complex **5** also had low sensitivity to the beam of fire. The investigation of the initiation ability of copper perchlorate complex **5** in blasting cap No 8 has shown that it cannot be ignited by the beam of fire of Bickford fuse[9].

Consequently, the assumed inhibiting effect of SH-group of the ligand in radical processes of burning and decomposition of complex perchlorates was experimentally supported.

The thermal stability of copper perchlorate complex **5** was investigated by a non-isothermal method (Derivatograph MOM-1500, temperature rise 5 K · min^{-1}). (see in Table 2).

Table 2　Analysis of the thermal stability of copper perchlorate complex 5

compound	mass loss /%	the interval of the effect /℃	*T* of the onset of decomposition /℃	T_{max} of the effect /℃	effect
$[Cu(C_2H_6N_6S)_2](ClO_4)_2$	–	20 – 152	–	–	–
$[Cu(C_2HN_3S)_2](ClO_4)$	37	152 – 315	200	222	exo
$[Cu(C_2HN_3)_2]$	28	315 – 428	350	362	exo
solid residue	35	> 430			

Table 2 shows that copper perchlorate complex **5** decomposes in two macrokinetic steps. Consequently, complex **5** has lower reactivity compared to copper complex **1** which decomposes in one macrokinetic step[3].

On the first macrokinetic step above 152 ℃ the weak N—N bonds are ruptured and, apparently, one ClO_4-anion oxidizes NH_2- and NH_2-NH-groups (calculated loss of mass ~35.4%). The second ClO_4-anion apparently oxidizes SH-groups (calculated mass loss ~29.6%). The solid residue contains unidentified copper-and 1,2,4-triazole-containing compounds. In all, copper complex perchlorate **5** has lower thermal stability as compared to copper complex perchlorate **1**[9], and Purpuld ligand has lower reactivity in the processes of thermal decomposition and Red-Ox reactions than that of 3(5)-hydrazino-4-amino-1,2,4-triazole ligand.

To find the thresholds of Q-switch laser initiation of perchlorate complexes **5 – 8**, some additional experiments were performed.

The results of investigation on the sensitivity of charges of **5 – 8** to pulses of neodymium containing glass IR-laser are presented in Table 3 ($\lambda = 1.06\ \mu m$, $\tau_q = 9$ ns, $d_{beam} = 0.5$ mm). The diameter of charges of compounds **5 – 8** equals to 5 mm, and their thickness is 2 mm. The accuracy of the resulting data is about 10%.

Table 3 Laser initiation of complexes 5 – 8

complex	E_{min}/J	H_{min}/ J · cm^{-2}	effect
$Cu(C_2H_5N_6S)_2(ClO_4)_2$	1.29×10^{-3}	5.16×10^{-1}	explosion
$Cd(C_2H_5N_6S)_2(ClO_4)_2$	1.53×10^{-1}	61.2	no ignition
$Co(C_2H_5N_6S)_2(ClO_4)_2$	1.53×10^{-1}	61.2	no ignition
$Ni(C_2H_5N_6S)_2(ClO_4)_2$	1.53×10^{-1}	61.2	no ignition

The threshold of initiation of copper perchlorate complex **5** is near 1.29×10^{-3} J. This value for compound **5** sensitivity to Q-switch IR-laser irradiation is equal to sensitivities of some industrial primary explosives (for example, mercury fulminate, lead styphnate, tetracene)[12]. Therefore compound **5** may be regarded as a promising safe light-sensitive explosive for laser detonators.

The thresholds of initiation of perchlorate complexes **6 – 8** exceed 61.2 J · cm^{-2} (which corresponds to the maximum power of the experimental Q-switch laser).

3 Mechanisms of Laser Initiation of Explosives

Initiation of explosives by laser radiation is in some respects distinct from other kinds of detonation excitation. Irradiation of an explosive with Q-switch laser pulse gives rise to a complex nonlinear thermal-chemical process in the substance. This process can be conventionally divided into the following stages: (i) light absorption by substance, (ii) mass and energy transfer, and (iii) chemical reaction of thermal decomposition. The mechanism of chemical transformation in the field of a high-power light wave depends on its energy.

The modem theories concerning the initiation o explosives are based on the concept of a hot spot—a region of intense local heating-up, directly responsible for the occurrence of fast reactions of thermal decomposition, including explosion. As the origin of a site may serve structural heterogeneities of the substance (point defects, vacancy aggregates, dislocations, phase boundaries, etc.), chemical impurities, and microinclusions appearing as a result of the non-stoichiometric composition of starting components in the synthesis of explosives, introduction of various additives in preparation, etc. In addition, defects may arise in the field of an intense light wave.

Laser initiation of organic high explosives by Q-switch laser pulse requires high energy (for example, PETN has the threshold of initiation by neodymium laser ~7.5 J · cm^{-2}[12]) and has two steps. The first step of initiation is crack formation on the surface of the explosive charge. The second step of laser initiation is plasma formation as a result of dielectric optical breakdown[13].

The primary explosives (for example, inorganic azides) have alternative mechanisms of initiation by the pulse of laser beam. They chemically decompose under pulse irradiation. Few mechanisms of laser initiation were suggested for inorganic azides[14]: chain branched reaction of laser initiation; photochemical reaction of laser initiation; shock wave initiated by the absorbed energy of laser pulse.

The realization of one or other initiation mechanism depends on the energy of Q-switch laser beam.

Unfortunately, detailed mechanisms of pulse laser initiation of energetic perchlorate complexes of *d*-metals with heterocyclic ligands are still unknown.

4 Conclusions

As it follows from the above data, the methyl group in 3-hydrazino-4-amino-5-methyl-1,2,4-triazole as ligand inhibit laser initiation of the investigated *d*-metal perchlorate complexes.

The SH-group in 3-hydrazino-4-amino-5-mercapto-1,2,4-triazole as ligand was experimentally supported to inhibit radical processes of burning and decomposition of complex perchlorate 5.

The sensitivity to Q-switch IR-laser irradiation of perchlorate complexes **5 – 8** is lower than the sensitivity to Q-switch IR-laser irradiation of perchlorate complexes **1 – 4**. Apparently, it is the result of changes in the mechanisms of interaction of perchlorate complexes with the laser beam.

The sensitivity of compound **5** to Q-switch IR-laser irradiation does not exceed the sensitivities of industrial primary explosives (for example, mercury fulminate has the threshold of initiation by Q-switch laser beam ~1000 mJ · cm^{-2} and lead styphnate- ~400 mJ · cm^{-2}[12]). Hence complex **5** is a promising safe light-sensitive explosive for laser detonators.

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