ISSN 1990-7931, Russian Journal of Physical Chemistry B, 2019, Vol. 13, No. 1, pp. 119–138. © Pleiades Publishing, Ltd., 2019.
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COMBUSTION, EXPLOSION, AND SHOCK WAVES

Energy-Saturated Metal Complexes

M. A. Ilyushin[a], *, A. A. Kotomin[a], and S. A. Dushenok[a]
[a] *SCTB Technolog, St. Petersburg, 192076 Russia*
**e-mail: explaser1945@yandex.ru*

Received April 12, 2018; revised July 13, 2018; accepted August 20, 2018

Abstract—A review of energetic coordination compounds (metal complexes) that show promise for application in safety initiation tools is conducted. Green substances meeting most environmental requirements, as well as light-sensitive compounds and their laser initiation are considered. Their chemical structures and properties are given. Methods for calculation of the single-crystal density and the speed of detonation of energy-saturated metal complexes are proposed.

Keywords: energy-saturated metal complexes, coordination compounds, safety primers, environmental friendliness, cobalt aminates, light-sensitive materials, laser initiation, single-crystal density, speed of detonation

DOI: 10.1134/S1990793119010238

INTRODUCTION

In the 20th century, lead azide, lead styphnate, and mercury fulminate were the main priming explosives (PEs) used to fill initiating agents (IAs); at the present time, these compounds are banned almost everywhere worldwide [1]. The use of dozens of millions of blasting caps (BC), electrical detonators (ED), and ignition caps (IC) have brought lead superecotoxicant into the environment in the amount of hundreds of kilograms per annum, thereby damaging both ecosystems and individuals [2]. The half-life of its elimination from bones is about 25 years. The lead pollution of land ecosystems is especially dangerous because lead extensively concentrates and is retained in soil, becoming transferred to plants and being extensively involved in food chains.

At the end of the 20th century, several countries accepted state programs for restriction and complete withdrawal of application of lead salts in civil IAs. In 2006, the researchers from the Los Alamos National Laboratory (United States) developed and published quite strict requirements for environmentally friendly (ecofriendly or green) energetic substances to replace lead azide and styphnate in civil BCs, EDs, and ICs.

In authors' opinion, an ideal green PE should meet the following six criteria: non-sensitivity to moisture and light, low sensitivity to mechanical exposure and static electricity charges for the purposes of reprocessability and transportation, thermal stability up to at least 200°C, long-storage chemical stability, the absence of group I toxicity metals, and the absence of perchlorate, which is likely to be a teratogen (causing teratism during prenatal development) and to have an adverse effect on the thyroid gland [3].

Laboratories worldwide extensively work on the synthesis and study of properties of PE for lead-free IAs. Some of their research data concerning energetic metal complexes are given in the present review.

1. COBALT AMINATES AS EXPLOSIVES FOR SAFE INITIATING AGENTS

In the second half of the 20th century, energetic metal complexes found practical application as explosives [4]. One reason for interest in energetic coordination compounds was the strengthening of requirements for the operational safety of blasting works. The call for safety increased upon the replacement of conventional high-sensitivity PEs in BC for less sensitive energetic coordination compounds, with an increase in the reliability of the detonator and its power transmission line, and in the use of a communication line between the power generator and the detonator that does not transmit and generate false initiating pulses in emergency.

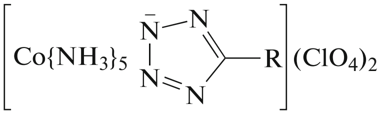
At the end of the 20th century, researchers in several countries studied the preparation and property investigation of *d*-metal complex salts with outer sphere having general formula of $M_x(L)_y(An)_z$ (M is the *d*-metal cation, L is ligand, and An is the acid anion, often acting as an oxidizer) as more safe than conventional PEs. The chemical structure of complex salts allows one to control their physicochemical, energetic, and performance characteristics within wide range and to design energetic compounds possessing high initiation power and, at the same time, a relative handling safety.

To predict the characteristics of energetic metal complexes in the design of their synthesis, a method for calculation of single crystal density of these compounds from contributions of their molecular fragments was developed [5, 6] and a method for calculation of the detonation speed of complex salts with oxidizing anion was built [7]. The latter combines the additive method for calculation of detonation parameters of explosive substances from contributions of chemical bonds and groups [8] and the method for calculation of detonation parameters of explosives with inert additives [9]. In the present review, the densities and rates of detonation of all metal complexes were calculated using the methods of A.A. Kotomin, which are described in details with examples in [10].

1.1. Cobalt Aminates with Tetrazole Ligands

Among coordination compounds recommended as explosives for initiation agents, of special note are cobalt(III) aminates containing substituted tetrazole anions as ligands (L) and outer-sphere perchlorate ions. For example, pentaamine (5-cyano-2H-tetrazolato-N^2) cobalt(III) perchlorate (CP) (**1**) and some of its analogs having a pronounced region of combustion-to-detonation transition were recommended as primers for safe low-voltage EDs [11].

These cobalt(III) pentaaminates have impact sensitivity on an impact machine considerably less than that of conventional PEs and are among brisant explosive substances (BES), such as pentaerythritol tetranitrate (PETN) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) [12]. The CP substance was found to be toxic, and its commercial production was halted in the United States [13]. In order to study this class of salts in details, metal complexes with monobasic, neutral, and dibasic tetrazoles with the following formulas have been synthesized [12]:



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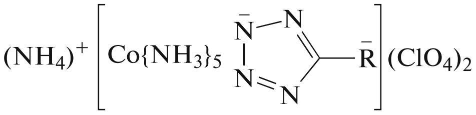

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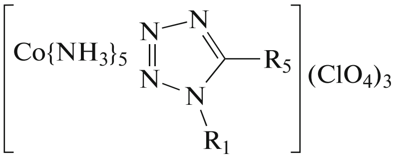


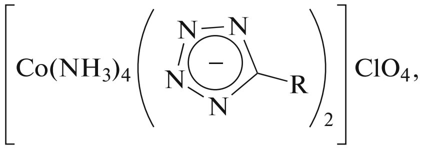
16, 17

Most studied cobalt(III) pentaaminates possess initiating ability upon testing in a BC tube No. 8. Their minimum charge with regard to RDX increases in the order **12** < **3** < **2** ~ **11** ~ **17** < **1** ~ **9** ~ **15** < 4 ~ **17** < **10**. The single crystal density of obtained perchlorates varies in a range from 1.83 (**14**) to 2.05 g/cm^3 (**10**). The calculated rates of detonation of salts **2**–**17** at these densities are in a range between 6.94 (**4**) and 8.03 km/s (**10**).

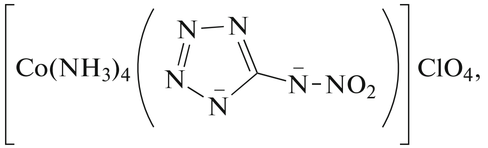
Among metal complexes given in Table 1, salt **3** is the most promising, since it successfully passed industrial tests as the main component of explosion transformer (PVP-1) in perforating-explosive equipment designed for execution of works in deep oil and gas wells [14, 15].

Tetraamine *cis*-bis(5-nitro-2H-tetrazolato-N^2) cobalt(III) perchlorate (BNCP, **18**) was proposed for the first time in 1986 as one of the most efficient and safe ESs for initiation agents [16]. Complex **18** is less sensitive to impact on an impact machine than PETN [17]. Using experience gained upon preparation and property investigation of cobalt pentaaminates with tetrazole ligands, cobalt tetraaminates with substituted tetrazoles were synthesized and studied. Properties of some of synthesized complexes are given in Table 2 [12].

All studied cobalt(III) tetraaminates were found to possess initiating ability in testing in BS tube No. 8. Their minimum charge with regard to RDX increases in the order: **18** < **23** < **19** < **24** < **22** < **20** < **21**. The single-crystal density of obtained perchlorates is in a range from 1.75 (**19**) to 2.03 g/cm^3 (**18**). The calculated speed of detonation of salts **18**–**24** at these single-crystal densities is in a range between 6.7 (**21**) and 8.1 km/s (**18**), respectively. Substances **18** and **24** are light-sensitive compounds, which are inflamed on exposure to laser radiation [18]:



18–20



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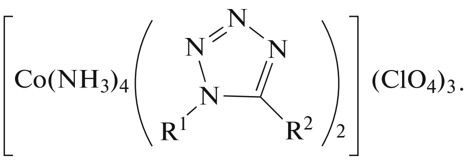
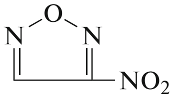
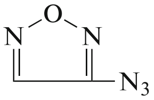
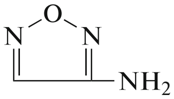
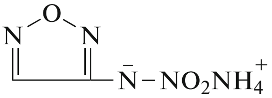


22–24

Table 1. Properties of cobalt(III) tetrazolate pentaminates

Complex	R_1	$R(R_5)$	ρ_{exp}, g/cm^3	ρ_{calc}, g/cm^3	$D_{\rho\ calc}$, km/s	$D_{\rho\ exp}$, km/s	T_{dec}, °C
1	–	$-CN$	1.96	1.96	–	7.18 (1.75)	288
2	–	$-H$	1.97	2.00	7.14 (1.97)	–	280
3	–	$-NO_2$	2.03	2.04	6.30 (1.61)	6.55 (1.61)	265
4	–	$-CH_3$	1.88	1.88	6.94 (1.90)	–	282
5	$-CH_3$	$=N-NO_2$	2.02	2.02	7.79 (2.02)	–	240
6	–	$-N=NO_2^-NH_4^+$	1.87	1.87	–	6.32 (1.52)	250
7	–	$-NH_2$	1.95	2.00	6.14 (1.62)	6.50 (1.62)	270
8	–	$-C(NO_2)_2^-NH_4^+$	1.88	1.88	–	6.32 (1.48)	201
9	–	$-CH_2N_3$	1.94	1.96	7.44 (1.94)	–	302 (explosion)
10	–	$-C(NO_2)_3$	2.05	2.02	8.03 (2.05)	–	132
11	–		1.97	2.02	7.76 (1.97)	–	280
12	–		1.95	1.97	7.71 (1.95)	–	198
13	–		1.93	–	7.34 (1.93)	–	280
14	–		1.83	1.87	7.42 (1.83)	–	255
15	–	$-Cl$	2.02	–	–	6.50 (1.50)	–
16	$-NH_2$	$-CH_3$	1.95	–	7.32 (1.95)	–	218
17	$-NH_2$	$-NH_2$	2.03	–	7.68 (2.03)	–	216

The numbers in parentheses are charge densities.

Table 2. Physicochemical and explosive properties of Co(III) tetrazolate tetraaminates

Complex	R, R_1, R_2	ρ_{exp}, g/cm^3	ρ_{calc}, g/cm^3	$D_{\rho\ calc}$, km/s	T_{dec}, °C	SS, % *
18	$R=NO_2$	2.03	–	8.1 (1.97)	269	8
19	$R=H$	–	1.86	6.9 (1.86)	239	64
20	$R=CH_3$	–	1.75	6.8 (1.75)	252	–
21	$R={}^-N-NO_2$	–	1.81	6.7 (1.81)	242	14
22	$R_1=H, R_2=NH_2$	–	1.90	7.1 (1.90)	238	10
23	$R_1=CH_3$, $R_2=NH_2$	1.90	–	7.5 (1.90)	234	8
24	$R_1=R_2=NH_2$	–	1.85	7.3 (1.85)	233	32

* Method for determination of shock sensitivity (SS) according to GOST 4545-88 (the load was 2 kg and the weight of ES was 20 mg). For reference, the SS of PETN is 12%.

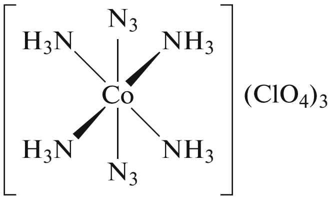
Table 3. Properties of complex **26**

Compound	ρ_{calc}, g/cm^3	$D_{\rho\ calc}$, km/s	T_{dec}, °C	SS, %
$[Co(NH_3)_5(4ATrz)](ClO_4)_3$	2.08	7.54 (2.00)	259	8

Among metal complexes given in Table 2, BNCP (**18**) which has found practical application in initiation systems in the United States is the most promising substance [1, 19].

1.2. Cobalt Aminates with Nitrogen Ligands

All known cobalt(III) bis-tetrazolate tetraaminates are *cis*-isomers. In a series of the *trans*-isomers of cobalt(III) tetraaminates with energetic ligands, *trans*-tetraaminediazido cobalt(III) perchlorate (**25**) was described in the literature [20]:



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This has attracted the attention of researchers as a low-toxicity substitution for lead azide in blasting caps. However, the conditions of synthesis and properties of this metal complex were not mentioned in report [20].

Pentaamine 4-(amino-1,2,4-triazole) cobalt(III) perchlorate ($[Co(NH_3)_5(4ATrz)](ClO_4)_3$, **26**) is an energetic metal complex with 4-amino-1,2,4-triazole (4ATrz) as the ligand [21]. Some properties of complex **26** are given in Table 3. The impact sensitivity of complex **26** is comparable with that of PETN and its efficiency is comparable with that of complex **3**, which confirms that the search for energetic substances designed for safe IAs is promising to be performed among cobalt(III) aminate perchlorates with 1,2,4-triazole ligands.

2. LIGHT-SENSITIVE COORDINATION COMPOUNDS AND THEIR LASER INITIATION

Laser initiation is a relatively new method for initiation of energetic materials (EM) being notable for increased efficiency. The laser initiation of EMs provides a high level of light detonator insulation from false pulse because random sources with a power sufficient for blasting of the detonator initiating charge are absent in the visual range. Light detonators are insensitive to electromagnetic blasts and static electricity charges [22–27].

Table 4. Time of initiation delay for charges of BNCP (**18**)

Particle size, μm	Delay, μs
77.29	505.8
23.42	521.9
11.71	377.4
2.29	350.6
0.85	326.7

Laser initiation can be used with success in many blasting works: explosion welding, die molding, hardening, and compaction. Rock blasting works require simultaneous or short-delay initiation of many light detonators through fiber optic communication lines. The use of fiber optic channels to transmit the laser pulse energy from a coherent source to light detonators in pyro automatic systems of space vehicles is considered as safe and reliable. For the perforation of deep oil and gas wells, it is reasonable to use heat-resistant fiber optic light detonators with a high susceptibility to laser pulse providing a reliable initiation of several dozen hollow BES charges [24].

2.1. Complex Cobalt Perchlorates

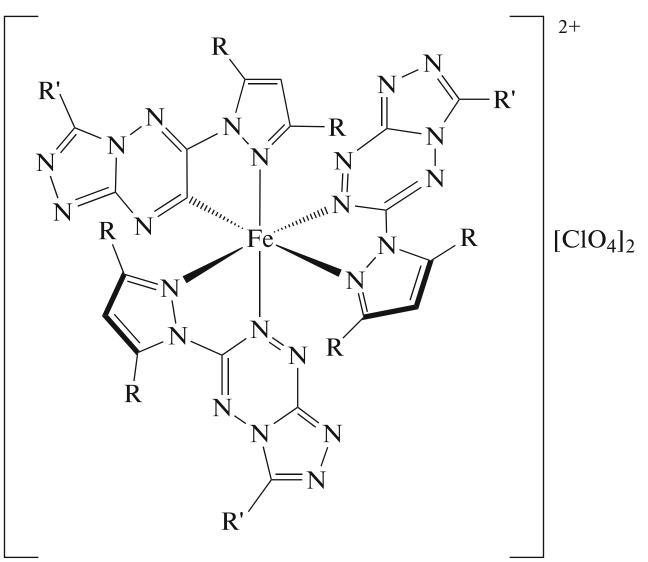
Among main elements of the laser initiation explosive train is light-sensitive EMs. To solve certain problems, inorganic azides and energetic metal complexes with different thresholds of monopulse or single pulse laser initiations were proposed as light-sensitive ESs for light detonators. For example, light detonators containing light-sensitive BNCP (**18**) charges are used with success in the pyro automatics of missile systems in the United States [28]. The delay time of BNCP charge ignition with a single laser pulse (τ = 700 μs) is from ~320 to ~500 μs depending on the crystal size of samples (Table 4) [29].

The mechanism of laser initiation of complex cobalt perchlorates has not been clarified. In [18], an attempt was made to estimate the effect of substituents in the tetrazole ring of BNCP analogs (Table 2) on their inflammability with the Neodymium laser beam under free-running lasing conditions (the wavelength was 1.06 μm, the pulse time was ~2 ms, the beam diameter was ~0.5 mm, and the energy was ~1.5 J). The studies showed that the charges of complexes **18**, **21**, and **24** detonated under experimental conditions, while complexes **19**, **22**, and **23** had initiation threshold above 1.5 J. Complex **20** burned smoothly after irradiation with a neodymium pulse laser. It is obvious that the $C-NO_2$, $C-N(NO_2)$, and $N-NH_2$ groups in the tetrazole ring decreases the initiation threshold of cobalt perchlorate complexes and the $C-NH_2$, $N-CH_3$, $C-CH_3$, and C–H groups increases its initiation threshold. The comparison of data on the optical properties of cobalt perchlorate complexes and the data from [12] showed that there is no direct relationship between the extinction coefficients of pressed charges of cobalt complexes and the thresholds of their initiation. The disadvantage of BNCP is its high initiation threshold on exposure to pulse laser.

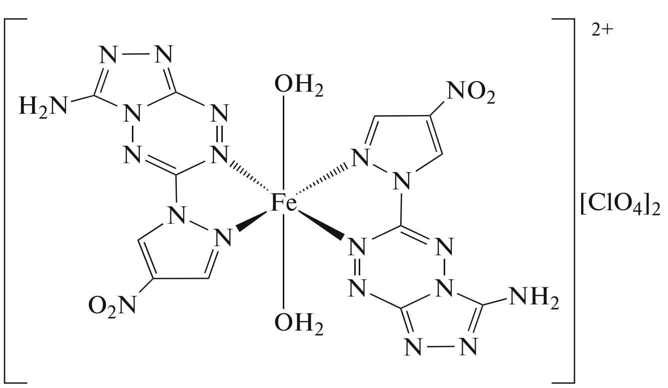
The authors of [30] state that tetraamine cobalt (III) perchlorate with the 1-methyl-5H-tetrazole (MTZ) ligand ($[Co(NH_3)_4(MTZ)_2](ClO_4)_2$, **27**) exhibits light-sensitivity and flames on exposure to single pulse of a laser InGaAs diode with a power of 45 W (the wavelength was $\lambda = 915$ nm, the pulse time was $\tau = 15$ ms, and the waveguide diameter was 400 μm). The initial decomposition temperature of complex **27** is about 201°C. This salt is sensitive to impact at the level of conventional PEs and requires further study.

2.2 Complex Iron(II) Perchlorates

The Los Alamos National Laboratory researchers showed that some of iron(II) perchlorate complexes with substituted tetrazines as the ligands are light-sensitive BESs [31, 32], for example, complex perchlorates



28 ($R'=R=CH_3$) [31]



29 [32]

Complex **28** has an initial decomposition temperature of 180°C and its impact and friction sensitivities are about three-fold lower than those of PETN, the oxygen balance of the complex is minus 66.4%. Complex **29** has an initial decomposition temperature of 174°C and its impact and friction sensitivities are, respectively, about 1.5- and 2.5-fold lower than those of PETN. The oxygen balance of salt **29** is minus 32.5%. (The initial decomposition temperature of PETN $T_{\text{in.dec}}$, according to [23] is 164.8°C and the oxygen balance is minus 10.1%). The laser initiation of complexes **28**, **29**, and PETN was carried out using an neodymium laser monopulse (the wavelength was $\lambda =$ 1064 nm, the pulse time was $\tau = 10$ ns, the waveguide diameter was 1 mm, and the pulse energy was 35 mJ). It was shown that, at a charge density of 0.9 g/cm^3, the threshold of initiation of complexes was 4.5 J/cm^2 and that of PETN under the same conditions was 6.4 J/cm^2. Consequently, the susceptibility of complexes **28** and **29** to laser monopulse and their initial temperatures are higher than those of PETN and their impact and friction sensitivities are lower, which makes these complexes promising for application instead of PETN in the laser analogs of exploding-bridgewire (EBW) detonators [33].

It should be noted that the use of laser analogs of EBW detonators in engineering is limited, since simultaneous initiation of several optical detonators require a high-power laser source which is not always available. Consequently, the search for light-sensitive substances having a threshold of initiation lower than those of complex cobalt(III) and iron(II) perchlorates is of current concern.

2.3. Complex Copper Perchlorate

In [1, 34–37], heavy and transition metal perchlorates complexes with hydrazine azoles were described. The choice of metal complexes was based on the positive enthalpy of formation of hydrazine azoles, a high oxidizing power of perchlorate ion, and a high ionization potential of metal cations, which should result in

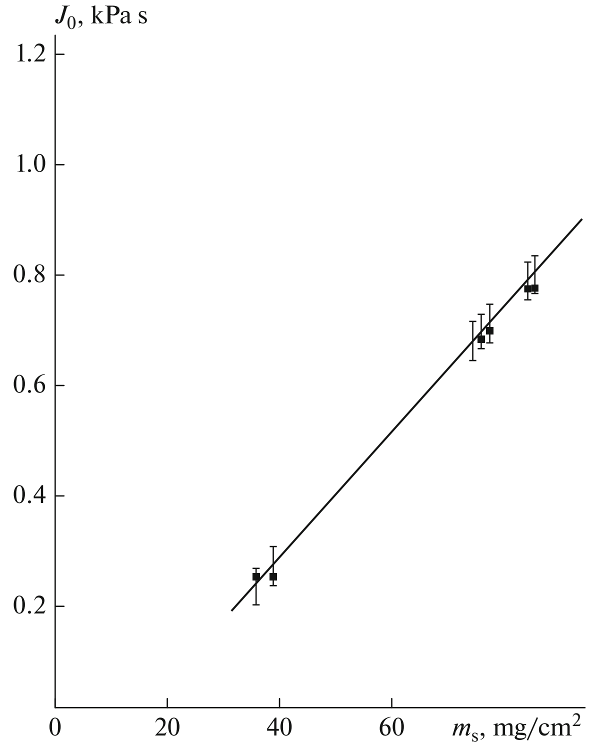
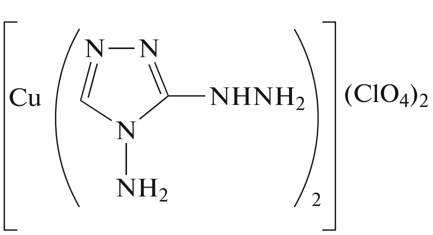


Fig. 1. Pulse of shock products (J) as a function of the specific gravity (m_s) of light-sensitive film composition samples based on the copper perchlorate complex VS-1.

preparation of energetic compounds with a short region of combustion-to-detonation transition.

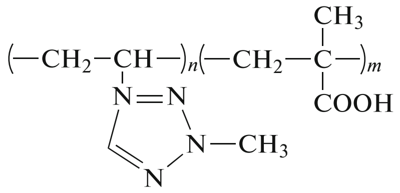
The study of the laser radiation susceptibility of copper(II), nickel(II), and cobalt(II) perchlorate complexes with 3(5)-hydrazino-4-amino-1,2,4-triazole showed that their laser monopulse sensitivity changes in accordance with the oxidizing power of the central metal ion expressed as the sum of ionization potentials $I_1 + I_2$. The higher this value is, the greater is the sensitivity of the metal complex to laser monopulse: Cu(II) > Cd(II) > Ni(II) > Co(II) [34, 38]. In [39, 40], the copper perchlorate complex



bis(3(5)-hydrazino-4-amino-1,2,3-triazole)
copper(II) perchlorate, **30**

was found to have an extremely low threshold of monopulse initiation by a neodymium laser (~10 mJ/cm^2).

Salt **30** has mechanical impact sensitivity comparable with that of conventional initiating ESs, which does not meet modern safety requirements for light-sensitive EMs. The mechanical impact sensitivity of copper perchlorate complex **30** was decreased by mixing it with polymers. The polymer matrix was the optically transparent polymer, energetic copolymer of 2-methyl-5-vinyltetrazole (~98%) and methacrylic acid (~2%):



Polymer PVMT

The impact sensitivity of obtained compositions decreased to that of modern BESs, such as PETN and CL-20, making them more safe under storage, transportation, and application conditions.

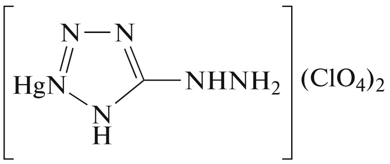
Thin films of the light-sensitive VS-1 composition (containing ~90% of complex **30** and ~10% of PVMT) were used to estimate the pulse of explosion products by the ballistic pendulum method. The laser one-pulse time was $\tau = 30$ ns and the wavelength was $\lambda = 1.06$ μm. The plots of the explosion product pulse (J_0) as a function of the specific gravity (m_s) were obtained for light-sensitive composition samples of copper perchlorate complex (Fig. 1), which showed that a portion of the VS-1 composition deflagrates upon laser initiation [35]. The pulse measurement accuracy was about ~±20%. The studies showed that the threshold of initiation of the VS-1 composition depended on the specific gravity of samples. A decrease in the VS-1 film thickness starting from m_s = 60–70 mg/cm^2 resulted in an increase in the threshold of initiation of the light-sensitive VS-1 with the neodymium laser monopulse. The films with a specific gravity of $m_s \leq 20$ mg/cm^2 were not initiated even upon monopulse irradiation at the energy density 15-fold higher than the critical value for millimeter samples (Fig. 2) [26].

The ignition delay time is one of the most important characteristics of light-sensitive energetic materials which governs to a large extent their potential application fields. It was shown that the ignition delay time of the VS-1 composition varied from 3.5 to 8 μs upon a two-fold change in the laser energy density, which is by an order of magnitude lower than that in BNCP (**18**). Using a solid-state neodymium laser operating under free-running lasing conditions (the wavelength was $\lambda = 1.06$ μm, the pulse time was $\tau = 2$ ms, and the laser beam diameter was 1 mm), the ignition thresholds of pressed samples of complex **30** and the light-sensitive VS-1 composition were determined [40] (Table 5).

The analysis of data given in Table 5 allows one to conclude that an about three-fold decrease in the initiation threshold of the VS-1 composition compared to the copper complex **30** is due to improvement in the conditions for formation of ignition foci. It follows from Table 5 that the threshold of initiation of the VS-1 composition with laser monopulse is by about two orders of magnitude lower (Fig. 2) than that upon initiation with the neodymium laser single pulse, which was to be expected because a portion of energy losses upon single pulse.

2.4. Complex Mercuric Perchlorate

5-Hydrazinotetrazole mercuric(II) perchlorate, which was studied as a model light-sensitive substance, demonstrated an extremely high susceptibility to laser monopulse:



31

The threshold of initiation of complex **31** with a neodymium laser (the wavelength was $\lambda = 1.06$ μm and the pulse time was $t = 30$ ns) was about 2.3 mJ/cm^2 [41]. Complexes of *d*-metals (Cu(II), Co(II), and Ni(II)) with the 5-hydrazino tetrazole ligand also possessed capability of being initiated with a neodymium laser single pulse ($W = 0.2$ J, $\lambda = 1.06$ μm, $\tau = 2$ μs, and the beam diameter was $d = 1$ mm), but their initiation threshold was higher [42].

Salt **31** is sensitive to external exposures at the level of conventional IESs and its minimum charge with regard to RDX in a BC tube No. 8 is ~ 0.015 g [41, 43]. Complex **31** was phlegmatized with PVMT. The sensitivity of obtained explosive VS-2 compositions (~90% of complex **31** and ~10% of PVMT) to mechanical exposures decreased to the level of high-power BESs, which made it possible to transport, store, and apply them in a relatively safe manner [44].

The minimum ignition delay time of the light-sensitive VS-2 composition depended on the power and conditions of laser radiation. It varied from 1 to 15 μs upon about a 10-fold decrease in the pulse energy density of the neodymium laser when irradiated with a single pulse having time of 30 μs and was ≤400 nm upon irradiation with the neodymium laser monopulse with a time of ~10 ns [41]. For irradiation of the VS-2 samples with continuous beam of a laser diode (the wavelength was $\lambda = 445$ nm, the radiation time was 2 s, and the laser diode power was 1 W), the ignition delay time was ~30 ms. With a decrease in the laser diode beam power to ≤0.25 W, the ignition delay time increased to ~400 ms [45, 46]. Consequently, the decrease in the power of the coherent radiation source from megawatts to portions of watt resulted in an increase in the ignition delay time of the VS-2 composition by six orders of magnitude.

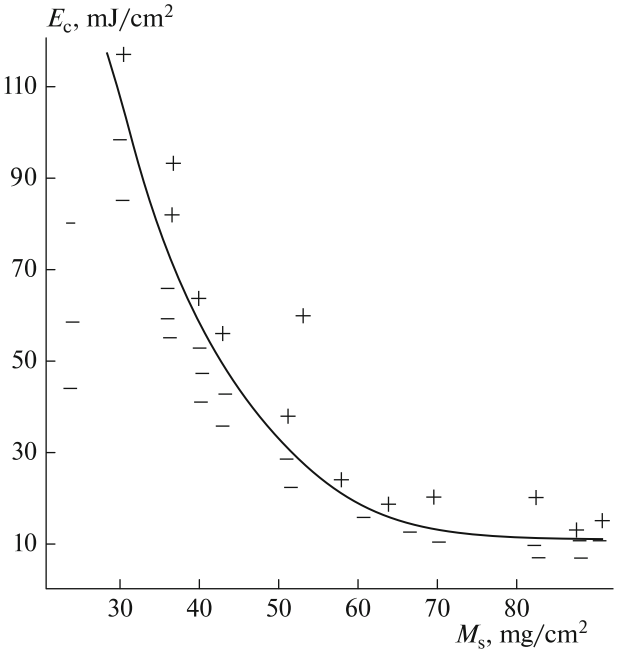
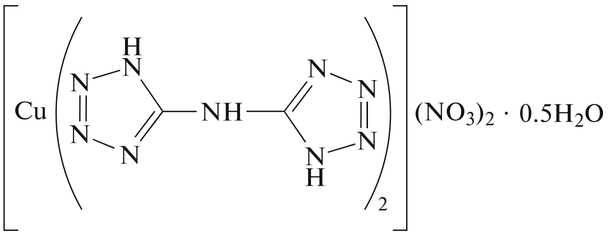


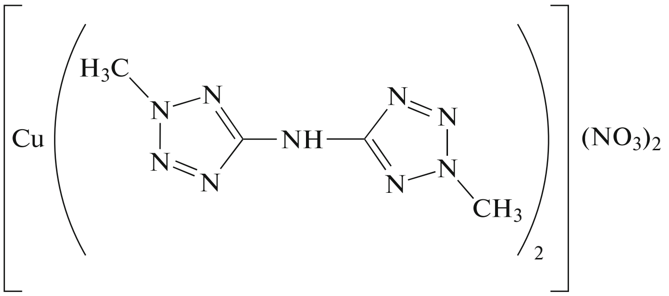
Fig. 2. Critical energy of initiation (E_c) as a function of the specific gravity of light-sensitive film composition based on the copper perchlorate complex VS-1 (M_s); (the laser beam diameter was 4.7 mm).

2.5. Metal Complexes Containing High-Enthalpy Ligands

The light-sensitive copper nitrate complexes



32



33

Table 5. Data from determination of the initiation threshold*

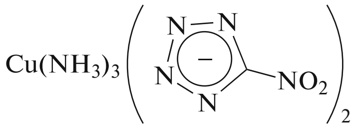
Sample	Energy flux density, *E*, J/mm^2
Charge of complex **30**	0.44
Charge of the VS-1 composition	0.135

*The data given are average for six parallel experiments. Mean experimental error was ±10%.

with tetrazole ligands were described in [47]. The ligand in complex **32** was 5,5'-(1H-tetrazol-5-yl)amine and the ligand in the copper complex **33** was 5,5'-bis(2-methyl-tetrazol-5-yl)amine. The methyl groups in the 5,5'-bis(2-methyl-tetrazol-5-yl)amine ligand decrease the impact sensitivity of complex **33**.

An attempt to record Raman spectra for complexes **32** and **33** resulted in explosion of the samples. The coherent radiation source was a solid-state Nd/YAG laser with a power of ~200 mW. Thus, low-toxicity copper complexes **32** and **33** require further studies as energetic light-sensitive substances for environmentally friendly optical initiating agents.

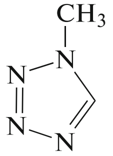
The tris-(ammine) copper(II) 5-nitrotetrazolate



34

is insensitive to electrostatic discharge, but highly sensitive to impact, friction, and coherent radiation of a green EM [48]. Complex **34** starts to decompose at $T_{\text{in.dec.}}$ ~245°C and is of potential interest as a lead-free initiating light-sensitive substance.

In [30], light-sensitive energetic metal complexes with 1-methyl-5H-tetrazole (MTZ) were obtained and studied:

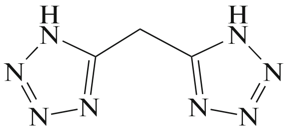


MTZ

Complexes **35**, **36**, and **38**–**41** were shown to be inflamed on exposure to single pulse of the laser InGaAs diode with a power of 45 W (the wavelength was $\lambda = 915$ nm, the pulse time was $\tau = 15$ ms, and the waveguide diameter was 400 μm) and complex **37** detonated under these conditions (Table 6).

Complexes **35**–**41** had no impact sensitivity at the level of PEs, this fact also concerns the products of cocrystallization with MTZ. The authors of [30] described for the first time the light-sensitive styphnic acid complex **41**. Complex **37** is the most promising among obtained substances and should be studied in optical initiation tools.

In [49], energetic transition metal complexes with di-(1H-tetrazol-5-yl)methane (5-DTM) were prepared and studied:



5-DTM

Complexes **42** and **43** were found to flame on exposure to laser diode single pulse with a power of 25 W (the pulse energy was 12 mJ, the wavelength was $\lambda = 940$ nm, and the pulse time was $\tau = 600$ μs), see Table 7.

These substances are sensitive to impact at a level of PEs. Salt **42** is of interest as a light-sensitive compound free of perchlorate ion.

In [50], the authors referred to an undeservedly forgotten efficient oxidizing anion for energetic metal complexes, chlorate ion ClO_3^-. The copper(II) chlorate complexes with 1-amino-1,2,3-triazole (1-ATRI), 4-amino-1,2,4-triazole (4-ATRI), 1-methyltetrazole

Table 6. Data from charge initiation of metal complexes

Complex	Formula	T_{endo}, °C	T_{exo}, °C	Effect from laser exposure
35	$[Fe(MTZ)_6](ClO_4)_2$	–	213	Combustion
36	$[Ni(MTZ)_6](ClO_4)_2$	–	271	Combustion
37	$[Cu(MTZ)_6](ClO_4)_2$	178	211	Detonation
38	$[Fe(MTZ)_6](ClO_4)_2 \cdot 2$ MTZ	111	215	Combustion
39	$[Ni(MTZ)_6](ClO_4)_2 \cdot 2$ MTZ	93	207	Combustion
40	$[Cu(MTZ)_6](ClO_4)_2 \cdot 2$ MTZ	78	206	Combustion
41	$[Cu(HTNR)_2(MTZ)_2]$	–	231	Combustion

Table 7. Data from charge initiation of metal complexes

Complex	Formula	T_{dec}, °C	Effect of laser exposure
42	$[Cu(NO_3)_2(5\text{-DTM})_2]$	148	Combustion
43	$[Cu(ClO_4)_2(5\text{-DTM})_2]$	233	Combustion

Table 8. Data from charge initiation of light-sensitive compositions

Complex	Formula	T_{dec}, °C	Ignition delay time, s
53	$[Co(CHZ)_3(ClO_4)_2]$	243	40.1×10^{-5}
54	$[Ni(CHZ)_3(ClO_4)_2]$	273	13.6×10^{-5}
55	$[Cu\ (ClO_4)_2(CHZ)_2]$	186	6.5×10^{-5}

(MTZ), 1-methyl-5-aminotetrazole (1-MAT), 2-methyl-5-aminotetrazole (2-MAT), 1,3-di(tetrazol-1-yl)propane (1,1-dtp), 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (1,2-dtp), 1,3-di(tetrazol-2-yl)propane (2,2-dtp), 1,1'-(propane-1,2-diyl)-bis(tetrazole) (*i*-dtp), and 1,4-di(tetrazol-1-yl)butane (dtb) were synthesized and studied.

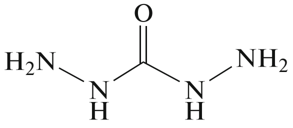
The following complexes $[Cu(ClO_3)_2(1\text{-ATRI})_4]$ (**44**), $[Cu(ClO_3)_2(MTZ)_4]$ (**45**), (1/2) $[Cu_2(4\text{-ATRI})_6](ClO_3)_2$ (**46**), $[Cu(ClO_3)(1\text{-MAT})_4]ClO_3$ (**47**), $[Cu(ClO_3)_2(H_2O)_2(2\text{-MAT})_2]$ (**48**), $[Cu(1,1\text{-dtp})_3](ClO_3)_2$ (**49**), $[Cu(ClO_3)_2(1,2\text{-dtp})_2]$ (**50**), and $[Cu(ClO_3)_2(dtb)_2]$ (**51**) detonate on exposure to the laser diode beam with an energy from 0.17 to 25.5 mJ. The properties of obtained salt are still under study; therefore, it is early to speculate on promising practical application of light-sensitive copper chlorate complexes with high-enthalpy azole ligands.

2.6. Metal Complexes with Hydrazine Derivatives, Carbohydrazides, Methylsemicarbazide, and 3-Amino-1-nitroguanidine

The fact that nickel hydrazinates with oxidizing anions have a short combustion-to-detonation transition region and can be used to initiate organic energetic substances has been known for about 100 years [1]. However, these compounds are inferior in efficiency to lead azide and were not considered promising. The search for environmentally friendly energetic compounds made researchers come back to this class of metal complex salts. Among promising lead-free energetic compounds capable of replacing lead azide in industrial BCs and EDs is tris(hydrazine)nickel(II) nitrate $Ni(N_2H_4)_3(NO_3)_2$ (**52**) [1].

Nickel hydrazinate **52** flames on exposure to pulse radiation of a CO_2 laser (with one-pulse energy of ~12.0 J/cm^2), which predetermines its using in optical initiation tools. An industrial process for the production of this energetic metal complex was elaborated in China in the 21th century. Unfortunately, the thermal stability (the flash point T_{fl} upon five-second delay is ~167°C) and initiating power (the weight of minimum charge with regard to PETN is ~150 mg) of complex **52** do not meet modern requirements for explosives of initiation tools. In addition, nickel is an active carcinogen. A relatively low mobility of this metal causes its sufficiently homogeneous distribution in natural media. Consequently, at high environmental content of nickel resulting from a large-scale application of complex **52** in civil IAs the unfavorable effect of this metal on living bodies will continue for a long time.

Some complexes with substituted hydrazines also possess properties of light-sensitive explosives. For example, the authors of [51] showed that transition metal perchlorate complexes with carbohydrazide (CHZ) as the ligand are initiated through a laser diode pulse [51]:



CHZ

Single pulse of a laser diode with a power density of 10^5 W/cm^2 (the wavelength was λ = 940 nm and the pulse time was τ = 400 μs) initiate compositions containing 5% of polyethylene and 95% of complexes **53**–**55** (Table 8).

Salts **53**–**55** are quite heat-resistant. The authors of [51] showed that the ignition delay time of these complexes depends on the nature of the central ion (and, possibly, on its ionization potential) and varies from 65 to ~400 μs, which makes these complexes promising IES for probable application in optical IAs.

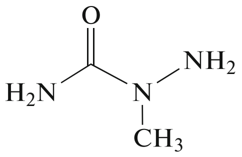
Some copper(II) and nickel(II) complexes containing methylsemicarbazide (MSC) as the ligand, which also can be considered as a hydrazine derivative, are light-sensitive ESs:

Table 9. Data from charge initiation of metal complexes

Complex	Formula	T_{endo}, °C	T_{exo}, °C	*E*, mJ	
				0.2	34
56	$[Cu(ClO_4)_2(MSC)_2]$	–	186	Detonation	–
57	$[Cu(N_3)_2(MSC)_2]$	–	121	Decomposition	–
58	$[Ni(MSC)_3](ClO_4)_2$	252	258	–	Detonation

Table 10. Data from charge initiation of metal complexes

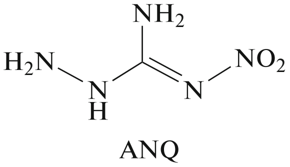
Complex	Formula	T_{dehydr}, °C	T_{exo}, °C	Effect from laser exposure
59	$[Co(ANQ)_2(H_2O)_2](ClO_4)_2$	170	176	Detonation
60	$[Cu(ClO_4)_2(ANQ)_2] \cdot (H_2O)_2$	120	134	Detonation
61	$[Ag(ANQ)_2]ClO_4$	–	148	Detonation


MSC

These complexes are initiated on exposure to the beam of a pulse laser InGaAs diode with a power of 45 W (the wavelength was λ = 915 nm, the pulse time was τ = 0.1 or 15 ms, and the waveguide diameter was 400 μm). The laser pulse energy was 0.2 mJ (0.1 ms) or 34 mJ (15 ms)] [52] (Table 9).

It follows from Table 9 that the nature of the metal cation has an effect on the threshold of laser pulse decomposition of MSC, while the oxidizing anion ClO_4^- in copper and nickel complexes provides a fast combustion-to-detonation transition. These complexes require further studies in order to determine their possible application fields.

The authors of [53] synthesized and studied a wide range of metal complexes with 3-amino-1-nitroguanidine (ANQ) and oxidizing anions, such as nitrate, perchlorate, dinitramide, and others (a total of 15 compounds):


ANQ

The ANQ ligand combines properties of EMs substituted hydrazine. Single pulse of a laser diode (the wavelength was λ = 940 nm and the pulse time was τ = 100 μs) initiated detonation in three complex perchlorates whose properties are given in Table 10.

Remaining 12 complexes were found to have low sensitivity to laser radiation. It is still early to discuss promising practical application of complexes **59**–**61**.

Finally, it should be noted that the searches for green energetic compounds among metal complexes are carried out in many countries. There are ways to solve this problem and certain successes have been achieved. However, an optimum solution to the design of non-polluting IAs has not been obtained.

3. METHODS FOR CALCULATION OF CHARACTERISTICS OF ENERGETIC METAL COMPLEXES

3.1. Method for Calculation of the Single-Crystal Density of Compounds from Contributions of Molecular Fragments

Energetic coordination compounds (energy-saturated metal complexes) have a specific chemical structure: they contain ligands of different type, different metal cations, and anions, as well as NH_3, $H_2N{-}NH_2$, H_2O, and other molecules. Therefore, known methods used to calculate organic compounds cannot be used for them.

The proposed method for calculation of the single-crystal density of energetic metal complexes of different type is based on the principle of additivity of contributions from molecular fragments [5, 6]. In general, a complex system of molecular fragment contributions to the molar volume has been developed for compounds with aliphatic, alicyclic, aromatic, and heteroaromatic ligands. Also, contributions of ionic fragments, organic, inorganic, different metal cations, as well as of ammonia, hydrazine, and water molecules were shown. Corrections for the interaction of fragments, structural type, and relationship between rings were determined, which allowed one to take into account more precisely a variety of chemical struc-

Table 11. Main contributions of fragments to the molar volume of energy-saturated metal complexes

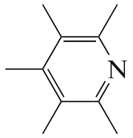
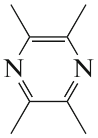
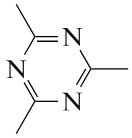
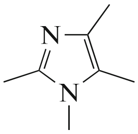
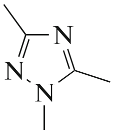
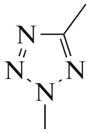
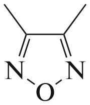
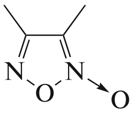
Fragment	V_i	M_i	Fragment	V_i	M_i
	28.06	74.06	$^{+}NH_4$	23.42	18.04
	32.39	76.06	$^{+}N_2H_5$	30.36	33.07
	35.30	78.05	$^{+}NH_3OH$	24.47	34.04
	25.79	64.05	$^{-}NO_3$	29.02	61.99
	28.68	66.04	$^{-}N_3$	27.59	42.02
	32.29	68.04	$^{-}C(NO_2)_3$	75.32	150.00
	33.94	68.03	$-\bar{C}(NO_2)_2$	40.21	104.00
	39.78	84.02	$^{-}N(NO_2)_2$	45.30	106.00
$(C_{ar,\,het}, N_{het})-CH_3$	22.04	15.03	ClO_3^-	35.58	83.45
$(C_{ar,\,het}, N_{het})-NO_2$	25.78	46.01	ClO_4^-	41.83	99.45
$-CH_2NO_2$	40.47	60.02	Na^+	8.48	22.99
$>CHNO_2$	24.72	59.01	Fe^{2+}, Fe^{3+}	3.56	55.85
$(C_{ar,\,het}, N_{het})-C(NO_2)_3$	80.17	150.00	Co^{2+}, Co^{3+}	2.41	58.93
$(C_{ar,\,het}, N_{het})-NH_2$	14.96	16.02	Cu^+, Cu^{2+}	8.22	63.54
(if the ring is substituted with NO_2)	11.74				
$(C_{ar,\,het})-C{\equiv}N$	25.27	26.02	K^+	15.91	39.10
$(C_{ar,\,het})-N_3$	30.78	42.02	Ag^+	8.54	107.87

Table 11. (Contd.)

Fragment	V_i	M_i	Fragment	V_i	M_i
$(\mathrm{N}_{het})\rightarrow\mathrm{O}$	5.41	15.99	Mn^{2+}, Mn^{3+}	4.44	54.94
$-\mathrm{CH}_2-$	14.77	14.03	Ni^{2+}	2.58	58.71
$-\underset{\mid}{\mathrm{CH}}-$	1.76	13.02	NH_3	15.91	17.03
$-\mathrm{NH}-$	6.03	15.01	$\mathrm{NH}_2-\mathrm{NH}_2$	24.77	32.05
$-\mathrm{OH}$	11.77	17.01	$\mathrm{H}_2\mathrm{O}$	15.90	18.02

Subscript *ar* denotes aromatic and subscript *het* denotes heterocyclic.

tures of compounds. The values of contributions and corrections were obtained from experimental densities of many organic substances from the reference and scientific literature.

In this method, structural components are molecular fragments whose contribution values have taken into account the interaction of elements within them and with neighbor atoms. The interaction of electron-withdrawing groups, the presence of hydrogen bonding, and steric factors are taken into account in both the contribution values of fragments, which depend on the surrounding, and different corrections. As a result, a general method to calculate the single-crystal densities of metal complexes containing C, H, N, O, S, F, Cl, Br, I, Na, K, Fe, Co, Cu, Pb, Ba, Li, Ag, Sr, Rb, Cs, Cd, Mn, Ni, Ce, Hg, and Zr.

The main contributions of molecular fragments to the molar volumes of compounds for energetic metal complexes are given in Table 11. The contribution values of all fragments are given in [10].

The developed method allows one to calculate the single-crystal density of compounds at the standard temperature of 20°C with a mean relative error of 1.5%. In this method, the single-crystal density of energetic metal complex is determined by the formulas

$$\rho_{\mathrm{sc}} = \frac{M}{V}, \quad M = \Sigma M_i, \quad V = \Sigma V_i + \Sigma \delta_i,$$

where ρ_{sc} is the single-crystal density of a substance, M is the molecular weight of a compound, M_i is the molecular weight of a fragment, V is the molar volume of a compound, V_i is the molar volume of a fragment, and $\Sigma\delta_i$ is the sum of corrections for interaction between fragments, structural type, and relation between rings.

Table 12 compares experimental and calculated single-crystal densities of energetic metal complexes with different chemical structures.

3.2. Method for Calculation of the Detonation Speeds of Metal Complexes

The main provisions of the method are set forth in [7, 10]. The essence of the developed method consists in partition of the energetic metal complex molecule into an active moiety (oxidizing anion and ligands) and an inert moiety (metal cation and crystallization water), combining on this basis the method for calculation of detonation parameters of ESs from contributions of chemical bonds and groups (for individual ESs) [8] and the method for calculation of detonation parameters for ESs witn inert additives [9, 55].

The calculation method shown in [9, 55] can be applied for mixtures of ESs with different types of inert additives (organic compounds, metals, oxides, salts, etc.). In terms of the proposed model, the complex compound cation is qualified as an ultrafine inert metal additive. Depending on the anion type, the ligand can be active or inert. In the case when an oxidizing anion, such as perchlorate anion, is present, the ligand is oxidized and, thereby, acts as a component of the active moiety. The crystallization water is an inert additive. This model of a complex compound does not take into account chemical bonding between the anion and the cation and introduces negligible error to calculation.

This method was developed on the basis of systemized experimental materials, including different-class compounds containing C, H, N, O, Cl, and S atoms, different metal cations, and oxidizing anions $[\mathrm{ClO}_4]^-$ and $[\mathrm{C(NO}_2)_3]^-$. The mean calculation error of the detonation speed was ±140 m/s [10].

The calculation scheme is described below.

A. Calculation of the Detonation Speed of an Explosive Moiety of a Complex Compound at a Density of 1.7 g/cm^3

Let us assume that the density of an explosive moiety is $\rho = 1.7$ g/cm^3 based on the fact that the density for the most of organic ESs varies in a range from 1.4 to 2.0 g/cm^3. Our assumption does not introduce an appreciable error, as next we calculate the speed of detonation for the explosive moiety at its true partial density in the charge.

The speed of detonation of the explosive moiety, D_{EM} (km/s), at its conventional density of $\rho = 1.7$ g/cm^3 is calculated by the formula

$$D_{EM} = 2.77 + \frac{\rho}{M_{EM}}(\Sigma n_i F_i + \Sigma n_j N_j), \tag{1}$$

where M_{EM} is the molecular weight of the explosive moeity; $\Sigma n_i F_i$ is the sum of contributions from groups of the explosive moeity of a complex ES (F_i is the contribution of a group and n_i is the number of groups of certain type); $\Sigma n_j N_j$ is the sum of contributions from chemical bonds between groups in the explosive moeity of a complex ES (bonds inside groups are taken into account in F_i); N_j is the contribution of a bond, and n_j is the number of bonds of certain type).

The contributions of groups and chemical bonds are given in Table 13 (α is the oxygen balance of the $C_aH_bO_cN_dF_eCl_fS_g$ explosive moiety in the molecule of a complex ES: $\alpha = \frac{c + e/2 + f/2}{2a + b/2}$).

B. Calculation of the Detonation Speed of the Explosive Moiety of a complex ES at Its Partial Density in the Charge

The partial density of the explosive moiety of a complex ES in the charge (ρ_{EM}, g/cm^3) is calculated by the formula

$$\rho_{EM} = \alpha_{EM}\rho_0, \tag{2}$$

where ρ_0 is the charge density of a complex ES, g/cm^3; and α_{EM} is the weight fraction of the explosive moiety in a complex ES which is determined from the relation

$$\alpha_{EM} = \frac{M_{EM}}{M_{ES}}; \tag{3}$$

where M_{EX} is the molecular weight of a complex ES.

The speed of detonation of the explosive moiety at density ρ_{EM} is in the linear relation:

$$D_{\rho_{EM}}[\text{km/s}] = D_{1.7} - M(1.7 - \rho_{EM}), \tag{4}$$

where $D_{1.7}$ is the speed of detonation of the explosive moiety at a density of 1.7 g/cm^3 (Eq. (1)); and M is a coefficient calculated for the $C_aH_bO_cN_dF_eCl_f$ explosive moiety by the formula:

$$M = \frac{1.1a - k_2 b + 7.6c + 8.1d + 7.2(e + f)}{0.1M_{EM}} \tag{5}$$

(at $[H] \le 3.5\%$ $k_2 = 3.0$; and at $[H] > 3.5\%$ $k_2 = 1, 3$).

C. Consideration of the Inert Moiety Effect. Calculation of the Detonation Speed of a Complex ES at a Charge Density

The final calculation step is determination of the detonation speed of a complex ES (D_{ES}, km/s) by the following formula:

$$D_{ES} = D_{\rho_{EM}} + \Sigma\Delta D_D, \tag{6}$$

where $\Sigma\Delta D_D$, km/s is the change in the detonation speed due to the presence of inert members (additives) in the molecule of a compound.

For inert moieties, such as ligands having no nitro, nitramine, nitrate, azide, or other explosophoric groups (if the metal complex molecules contain no oxidizing anions) or crystallization water, the ΔD_D value is determined by the formula:

$$\Delta D_D = 10^{-4} A_D^2 \frac{\beta\rho_0}{\rho_D}, \tag{7}$$

β is the weight fraction of the inert moiety in the molecule of a complex ES; ρ_D is the density of the inert moiety, g/cm^3; and A_D is the number of gram atoms of elements per 1 L of the inert moiety, g-at/L. The parameter A_D correlates with the speed of shock wave in the inert moiety material.

The parameter A_D is calculated by the formula

$$A_D = 10^3 \frac{N}{M_D}\rho_D, \tag{8}$$

where N is the number of atoms in the inert moiety of a metal complex and M_D is the molecular weight of the inert moiety (additive).

For cations of complex ESs, ΔD_D is calculated by the formula

$$\Delta D_D\ \text{km/s} = a(b - \rho_D)\frac{\beta\rho_0}{\rho_D}, \tag{9}$$

where ρ_D is the density of a cation (metal), g/cm^3; β is the weight fraction of a cation in the molecule of a complex ES; a is a coefficient equal to 1.125 (km/s)/(g/cm^3); and b is a coefficient equal to 4.0 g/cm^3 (the values of coefficients a and b are taken for ultrafine metals with a size less than 10 μm from [9, 55]).

Tables 14 compares experimental values [10, 12] and values calculated according to the proposed method for the rates of detonation of several energetic metal complexes. For all cobalt(III) tetrazole pentamminates given in Table 1, except for pentammine (5-cyano-2H-tetrazolato-N^2) cobalt(III) perchlorate, we determined the speed of detonation of compressed charges with a diameter of 100 mm by the ionization gage method.

Table 12. Experimental and calculated densities of single crystals of various energy-saturated metal complexes

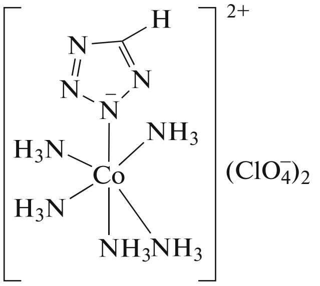
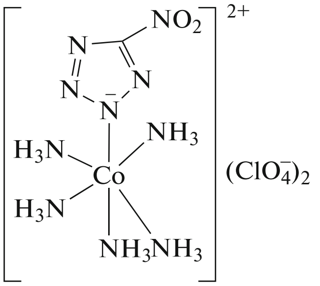
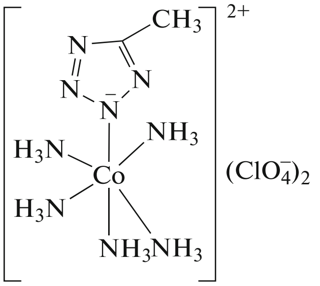
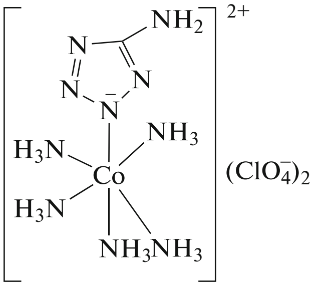
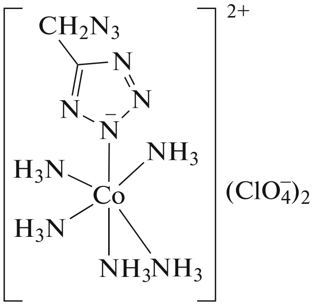
Ser no.	Compound	Structural formula	Single crystal density, g/cm^3	
			experiment	calculation
1	Pentaamine (2H-tetrazolato-N^2) cobalt(III) perchlorate $CoCH_{16}O_8N_9Cl_2$		1.97 [54]	2.00
2	Pentaamine (5-nitro-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoCH_{15}O_{10}N_{10}Cl_2$		2.03 [54]	2.04
3	Pentaamine (5-methyl-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoC_2H_{18}O_8N_9Cl_2$		1.88 [54]	1.88
4	Pentaamine (5-amino-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoCH_{17}O_8N_{10}Cl_2$		1.95 [54]	2.00
5	Pentaamine (5-methylazido-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoC_2H_{17}O_8N_{12}Cl_2$		1.94 [54]	1.96

Table 12. (Contd.)

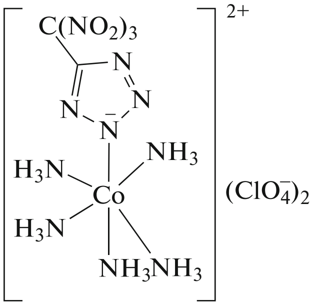
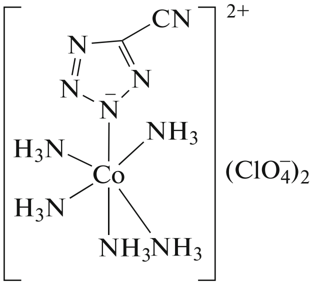
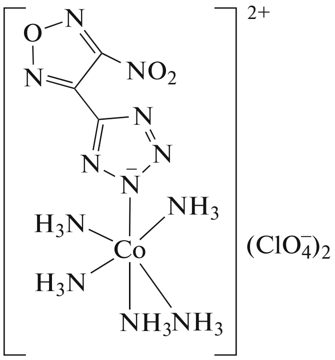
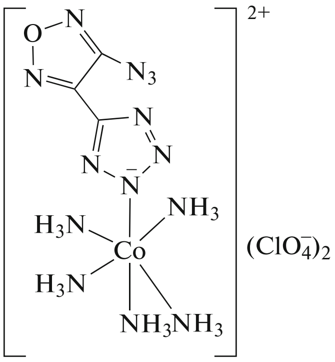
Ser no.	Compound	Structural formula	Single crystal density, g/cm^3	
			experiment	calculation
6	Pentaamine (5-trinitromethyl-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoC_2H_{15}O_{14}N_{12}Cl$		2.05 [54]	2.02
7	Pentaamine (5-cyano-2H-tetrazolato-N^2) cobalt(III) perchlorate (CP) $CoC_2H_{15}O_8N_{10}Cl_2$		1.96 [54]	1.96
8	Pentaamine (5-nitrofurazano-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoC_3H_{15}O_{11}N_{12}Cl$		1.97 [54]	2.02
9	Pentaamine (5-azidofurazano-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoC_3H_{15}O_9N_{14}Cl_2$		1.95 [54]	1.97

Table 12. (Contd.)

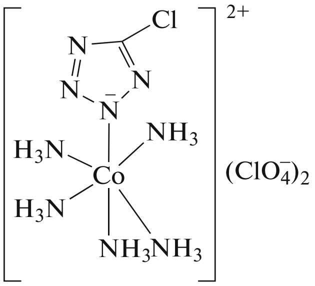
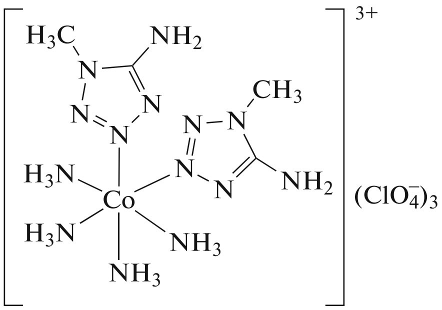
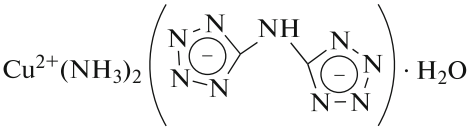
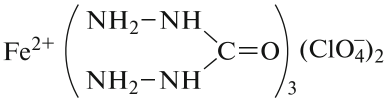
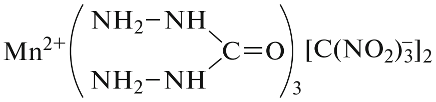
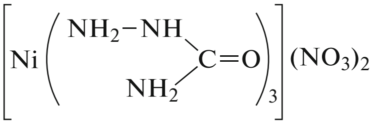
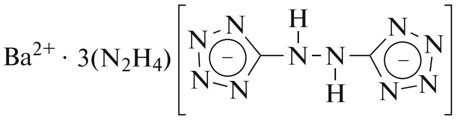
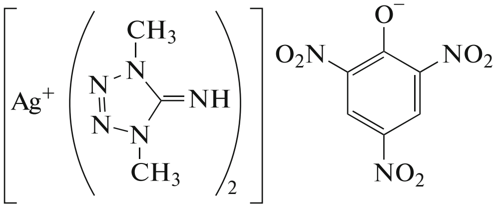
Ser no.	Compound	Structural formula	Single crystal density, g/cm^3	
			experiment	calculation
10	Pentaamine (5-chloro-2H-tetrazolato-N^2) cobalt(III) perchlorate $CoCH_{15}O_8N_9Cl_3$		2.02 [54]	2.03
11	Tetraamine bis(2-methyl-5-amino-2H-tetrazol-N^3) cobalt(III) perchlorate $C_4H_{22}O_{12}N_{14}Cl_3Co$		1.90 [1]	1.89
12	[Diammine-amino-bis-5,5'-(tetrazolato)] copper(II) monohydrate $C_2N_{11}H_9OCu$		1.953 [3]	1.94
13	Tris(carbohydrazide) iron(II) $C_3H_{18}N_{12}O_{11}Cl_2Fe$	 $Fe^{2+}\left(\begin{matrix}NH_2{-}NH\\NH_2{-}NH\end{matrix}\!\!>C{=}O\right)_3(ClO_4^-)_2$	1.967 [3]	2.01
14	Tris(carbohydrazide) manganese(II) nitroformate $C_5H_{18}N_{18}O_{15}Mn$	 $Mn^{2+}\left(\begin{matrix}NH_2{-}NH\\NH_2{-}NH\end{matrix}\!\!>C{=}O\right)_3[C(NO_2)_3^-]_2$	1.867 [3]	1.90
15	Tris(semicarbazide) nickel(II) nitrate $NiC_3H_{15}O_9N_{11}$	 $\left[Ni\left(\begin{matrix}NH_2{-}NH\\NH_2\end{matrix}\!\!>C{=}O\right)_3\right](NO_3)_2$	1.863 [3]	1.88
16	Tris(hydrazine) barium(II) (hydrazino-N,N'-di-5,5'-tetrazolate) $C_2H_{14}N_{16}Ba$		2.109 [3]	2.13
17	Bis(1,5-dimethyl-1H-tetrazoloimine) silver(I) picrate $C_{12}H_{16}N_{13}O_7Ag$		1.845 [3]	1.83

Table 12. (Contd.)

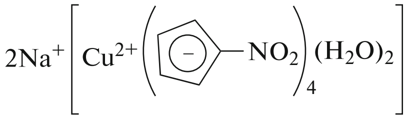
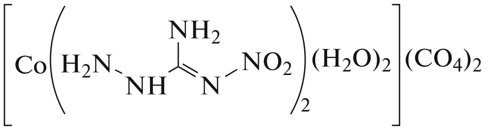
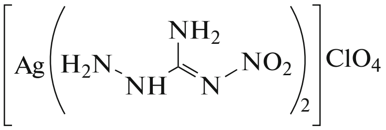
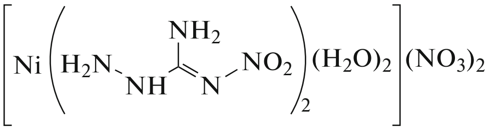
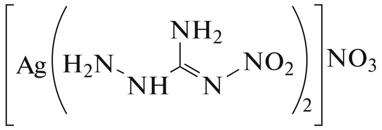
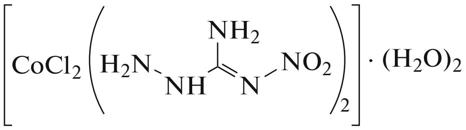
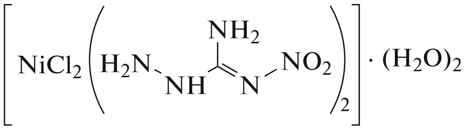
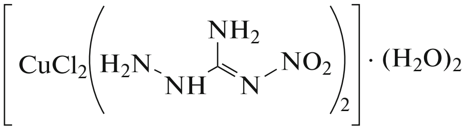
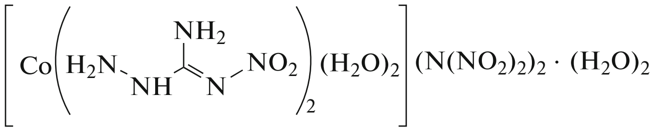
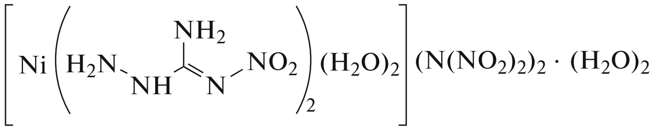
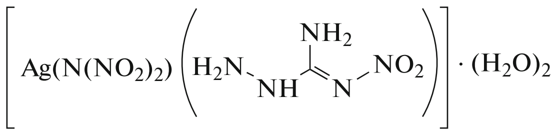
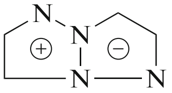
Ser no.	Compound	Structural formula	Single crystal density, g/cm^3	
			experiment	calculation
18	Diaqua-tetrakis(5-nitrotetrazolato) copper(II) disodium $Na_2CuC_4H_4O_{10}N_{20}$		2.10 [1]	2.08
19	Di-aqua-bis(3-amino-1-nitroguanidine) cobalt(II) perchlorate $CoC_2H_{14}O_{14}N_{10}Cl$		2.068 [53]	2.07
20	Bis(3-amino-1-nitorguanidine) silver(I) perchlorate $AgC_2H_{10}O_8N_{10}Cl$		2.316 [53]	2.34
21	Di-aqua-bis(3-amino-1-nitorguanidine) nickel(II) nitrate $NiC_2H_{14}O_{12}N_{12}$		2.011 [53]	1.97
22	Bis(3-amino-1-nitroguanidine) silver(I) nitrate $AgC_2H_{10}O_7N_{11}$		2.235 [53]	2.30
23	[Bis(3-amino-1-nitroguanidine)-dichloro]coblat(II) dihydrate $CoC_2H_{14}O_6N_{10}Cl_2$		1.927 [53]	1.93
24	[Bis(3-amino-1-nitroguanidine)-dichloro] dihydrate nickel(II) $NiC_2H_{14}O_6N_{10}Cl_2$		1.950 [53]	1.93
25	[Bis(3-amino-1-nitroguanidine)-dichloro] dihydrate copper(II) $CuC_2H_{14}O_6N_{10}Cl_2$		1.945 [53]	1.90
26	[Bis-dinitroamido diaqua-bis-(3-amino-1-nitroguanidine)] dihydrate cobalt(II) $CoC_2H_{18}O_{16}N_{16}$		1.964 [53]	1.96
27	[Bis-di-nitroamido di-aqua-bis(3-amino-1-nitroguanidine)] dihydrate nickel(II) $NiC_2H_{18}O_{16}N_{16}$		1.982 [53]	1.96
28	[(3-Amino-1-nitroguanidine)-di-nitroamido] monohydrate silver(I) $AgCH_7O_7N_8$		2.456 [53]	2.51

Table 13. Contributions of chemical bonds and groups

No.	Group	Contribution F_i	No.	Bond**	Contribution N_j
1	C*	6.6	1	C−C	13.4
2	CH	−8.4	2	C=C	−1.6
3	CH_2	−0.9	3	C−N	4.4
4	CH_3		4	C=N	39.6
	at [H] ≥ 3.8%	11.5	5	C−O	15.5
	at [H] < 3.8%	1.5	6	C=O	5.5
5	N*	8.8	7	N−O	29.3
6	NH	12.5	8	N=O	
7	NH_2	21.4		at $\alpha < 1.0$	94.0
8	$^+NH_3$	34.8		at $\alpha > 1.0$	43.2
9	$^+NH_4$	43.2	9	N → O	38.6
10	O*	15.0	10	N−N	52.1
11	OH	19.6	11	N=N	49.8
12	F*				
	at $\alpha < 1.0$	7.5	12	$\overset{\vert}{\underset{\vert}{-N^{\oplus}-}}\ \overset{\ominus}{NO_3}$	30.8
	at $\alpha > 1.0$	1.0			
13	Cl*	7.5	13	$\overset{\vert}{\underset{\vert}{-N^{\oplus}-}}\ \overset{\ominus}{C}(NO_2)_3$	28.8
14	S*	15.0	14	$\overset{\vert}{\underset{\vert}{-N^{\oplus}-}}\ \bar{O}Pic$	20.1
15	N=N	163.9			
16	$\underset{\substack{\downarrow\\ O}}{N{=}N}$	166.2	15	$\overset{\vert}{\underset{\vert}{-N^{\oplus}-}}\ \overset{\ominus}{N}(NO_2)R$	23.0
17	C≡N	169.7	16	$\overset{\vert}{\underset{\vert}{-N^{\oplus}-}}\ \overset{\ominus}{N_3}$	−11.1
18		144.6			
19	N_3		17	C−F	34.5
	at $\alpha > 0.35$	167.0	18	N−F	
	at $\alpha < 0.35$	190.3		at $b \geq e$ and $\alpha > 0.2$	74.8
20	NO_2			at $b \geq e$ and $\alpha < 0.2$	90.7
	at $\alpha < 0.35$	185.1		at $b < e$ $(b = 0)$	$30.8 + 44b/e$
	$0.35 \leq \alpha \leq 1.0$	175.8	19	C−Cl	26.2
	$1.0 < \alpha \leq 1.45$	$175.8 - 66(\alpha - 1.0)$	20	C−S	15.8
	$1.45 < \alpha \leq 1.55$	$146.1 - 229(\alpha - 1.45)$	21	S−O	89.3
	$1.55 < \alpha \leq 3.5$	123.2	22	S=O	64.6
	$\alpha > 3.5$	101.6	23	$\overset{\vert}{\underset{\vert}{-N^{\oplus}-}}\ \overset{\ominus}{ClO_4}$	32.7
21	NO_3^-				
	at $\alpha \leq 1.0$	209.2			
	at $\alpha > 1.0$	206.7			
22	ClO_4^-				
	at $\alpha \leq 0.2$	514.7			
	$0.2 < \alpha \leq 0.5$	309.8			
	$0.5 < \alpha \leq 1.0$	278.7			
	$1.0 < \alpha \leq 1.5$	269.2			
	$\alpha > 1.5$	227.2			

*Atom is considered as a group for all structures.

**Contributions are directly related to chemical bonds between atoms excluding atoms itself.

Table 14. Rates of detonation for some of energetic metal complexes

No.	Compound	Density, g/cm^3 (experiment)	Speed of detonation, km/s	
			experiment	calculation
1	Pentaamine (5-Cyano-2H-tetrazolato-N^2) cobalt(III) perchlorate	1.50	6.28	6.36
		1.65	6.82	6.82
		1.86	7.58	7.47
2	Aquapentaamine cobalt(III) perchlorate	1.702	5.69	5.59
3	Ammonium pentaamine (5-nitramino-2H-tetrazolato-N^2) cobalt(III) perchlorate	1.523	6.32	6.33
4	Aqua-tetrakis(4-amino-1,2,4-triazole) copper(II) perchlorate	1.60	6.61	6.64
5	Pentaamine (5-nitro-2H-tetrazolato-N^2) cobalt(III) perchlorate	1.613	6.55	6.30

CONCLUSIONS

Environmentally friendly (green) energy-saturated metal complexes and compositions on their basis are promising energetic materials for application in different fields. Many laboratories worldwide are working on the synthesis and property investigation of lead-free priming explosives. Some ways to solve this problem have been envisaged. Some successful research data have been given in the present review. However, an optimum solution to the design of non-polluting initiation tools has not been found.

Light-sensitive green coordination compounds and compositions are promising for the design of optical initiating agents. BNCP is the most known and has found practical application in the initiation systems in the United States.

The studies performed in Russia showed that the light-sensitive VS-2 composition based on the mercuric perchlorate complex could be applied in optical detonators. It was found experimentally by the example of this composition that a decrease in the laser beam energy (power) increases its ignition delay time. This conclusion is important from a practical perspective in the design of laser initiation tools.

To predict the characteristics of energy-saturated metal complexes when designing their synthesis, methods to calculate the single crystal density of these compounds from contributions of molecular fragments and the detonation speeds of complex salts with oxidizing anion have been developed.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (projects no. 16-29-01056-ofi_m and no. 17-03-00566).

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Translated by K. Utegenov