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Coordination Complexes as Inorganic Explosives for Initiation Systems

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Abstract: The study of the synthesis of coordination compounds in the series of perchlorates of d-metals containing polynitrogen heterocyclic ligands is presented in the following report. The major part of the report is also devoted to the investigations of properties of the compounds obtained and their applications in safe electric and laser detonators.

Key words: inorganic chemistry; complex; inorganic explosive; initiation system; Laser
CLC number: O61; TQ563 **Document code**: A

1 Introduction

Coordination complexes of d-metals represent an interesting class of explosives for detonators which are more safe than traditional ones[1]. Co(Ⅲ) pentaamminates and tetraamminates containing 5-R-tetrazoles as ligands are unique explosives that combine properties of primary and high explosives. As the result, investigations of the sensitivity of energetic complex salts to laser pulse radiation are of great theoretical and general interest. Energetic coordination compounds possessing high sensitivity to laser pulse are used in medicine, processing of metal surfaces, generation of profiled shock waves, mining and airspace technologies[2,3]. They have been used in military and industrial safe detonators[4,5].

2 Experimental

The above coordination complexes were synthesized by the reaction of perchlorate of d-metals with substituted tetrazoles, 1, 2, 4-triazoles and pyrazoles in diluted acid media at elevated temperatures. Detonation velocities for the salts were determined by ionization method. Densities of the complex salts were measured by pycnometric method. Derivatograph MOM "E. Paulic, J. Paulic, L. Erdey" (Hungary) was used to perform differential thermal analysis of the salts. The heating rate of the samples was 5 K · min^{-1}, masses of the complexes were 10 ~ 20 mg. IR spectra of the complexes were recorded in Nujol on a "Bruker-IFS-113" spectrometer (Germany). Mass spectra of decomposition products of the complex salts were registered on a MX-1310 spectrometer(USSR) under the electron impact energy of 70 eV. UV spectra of the complexes were recorded on a SF-46 spectrometer(USSR). NMR H^1 spectra of the complexes were recorded on a "Perkin-Elmer R-12" (UK) spectrometer (60 MHz), the samples of the complex salts were dissolved in DMSO d_6, HMDS was used as standard.

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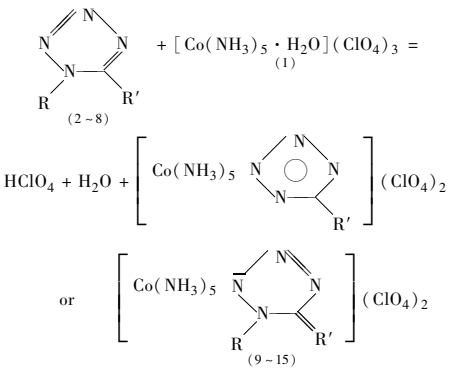
3 Results and discussion

Complexes of tetrazolatopentaammincobalt(Ⅲ) perchlorates were synthesized by reaction:



The acidity of the medium does not effect the kinetic parameters. The ionic strength of solution also does not influence the kinetic data. So it may be concluded that tetrazoles take part in the process in the neutral form; proton elimination takes place during the step that does not

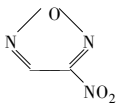
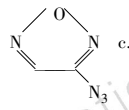
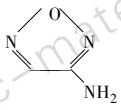
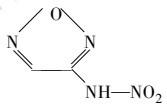
effect the total rate of the reaction. The reaction can be adequately described by the mechanism of simultaneous substitution.

Using the method of mathematical planning of experiment allowed us to optimize the reaction conditions. The processes of thermal decomposition of these salts comprise a problem of general importance. The thermal decomposition of Co(Ⅲ) pentaamminates with 5-R-tetrazoles as ligands is found to be subject to metal ion catalysis. Derivatographic investigations show the thermal decompositions of perchloric complexes 12 ~ 14, 16 ~ 20 occur by several steps. For most of the complexes the thermal decompositions start at temperatures over 200 ℃. The number of macrokinetic steps of decomposition depends on the nature of 5-R-substituents in the tetrazole ring. Mass-spectrometric investigations of the thermal decomposition of these complexes show that the perchlorate ion takes part in the process of oxidation of ligands at the final steps of decomposition. The main gaseous products decomposed these complexes are molecular nitrogen, nitrogen oxides, carbon oxides, water, hydrogen chloride and ammonia. The gaseous products also include traces of HCN. A minor amount of HN_3 can be identified as well. The ratio of the gaseous products decomposed depend on the nature of substituents at the ring.

Characteristics of the perchlorate complexes are given in Table 1.

Table 1 Characteristics of the perchlorate complexes

Entry	R	R′	$\rho_{exp.}$ /g · cm^{-3}	$D_{\rho calc.}$ /km · s^{-1}	$D_{\rho exp.}$ /km · s^{-1}	$T_{decomp.}$ /℃
9	CH_3	—$NHNO_2$	2.02	7.79 (2.02)	–	240
10	–	—$NHNO_2$	1.87	–	6.33 (1.52)	250
12	–	—NH_2	1.95	6.14 (1.62)	6.50 (1.62)	270
13	–	—CH_3	1.88	6.94 (1.90)	–	282
14	–	—H	1.97	7.14 (1.97)	–	280
15	–	—$CH(NO_2)_2$	1.88	–	6.32 (1.48)	201
16	–	—NO_2	2.03	6.30 (1.61)	6.65 (1.61)	265
17	–	—CH_2N_3	1.94	7.44 (1.94)	–	302(expl)
18	–	—$(NO_2)_3$	2.05	8.03 (2.05)	–	132
19	–	a	1.97	7.76 (1.97)	–	280
20	–	b	1.95	7.71 (1.95)	–	198
21	–	c	1.93	7.34 (1.93)	–	280
22	–	d	1.83	7.42 (1.83)	–	255

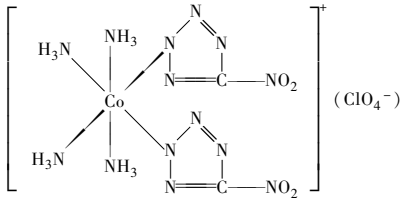
Notes: a.  b.  c.  d. 

Some complexes show an initiating ability when used in the detonator 8#. Their minimum initiating charge increases in the sequence of compounds: (20) < (16) ~ (19) < (14) < (17) < (13) < (18).

The densities of monocrystals of these complexes vary from 1.83 g · cm^{-3} (22) to 2.05 g · cm^{-3} (18). The calculated detonation velocities for salts 9 ~ 21 at the densities of monocrystal lie between 6.94 km · s^{-1} (13) and 8.03 km · s^{-1} (18).

Among the above salts, complex 16 has the best performance. A pulse convertor using the charge of complex (16) has been developed by researchers of the Saint-Petersburg State Institute of Technology and MO ANPF "Geofizica". This convertor has been successfully used as a perforating charge for oil and gas bore-holes.

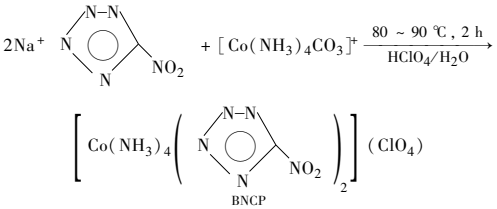
Perchlorate tetraamine-*cis*-bis (5-nitro-2*H*-tetrazolate-N^2)cobalt(Ⅲ) (BNCP) (23) was suggested at 1986 as one of the most efficient explosives for the system of initiation.



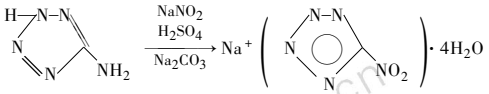
BNCP charges in blasting caps decompose with fast transition from ignition to detonation playing the role of both primary and secondary explosives (EC).

The density of BNCP monocrystals is 2.05 g · cm^{-3}, the calculated detonation velocity at density 1.97 g · cm^{-3} approaches 8.1 km · s^{-1}, the temperature of the onset beginning of intensive decomposition is 269 ℃, the minimum initiation charge for RDX in blasting cap 8# is about 50 mg, the time of transition from ignition to detonation ~10 μs, the heat of thermal decomposition is 3 319 J · g^{-1}.

BNCP complexes were synthesized by reaction:



The yield of compounds (23) was 60% ~70%. In the synthesis of complex (23) was used the sodium salt of 5-nitrotetrazole, prepared by the Sandmeyer reaction from 5-aminotetrazole:



The quality of BNCP depends on the purity of the sodium salt of 5-nitrotetrazole. The sodium salt of 5-nitrotetrazole can contain sodium nitrite ($NaNO_2$) as a natural admixture. In case of the incomplete removal of NO_2^- it may be presented as a ligand competing with the nitrotetrazolato-ion. That's why, special attention was paid to elaborate the method of purification cleaning and, as a result, the sodium salt of 5-nitrotetrazole was obtained with the purity of 98%.

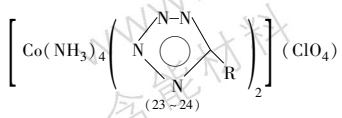
The effective means of thermal activation of chemical reactions is the method of microwave heating. The synthesis of (23) under conditions of microwave heating at the boiling temperature of solution (102 ℃) during 1 hour resulted in 80% yield of the product.

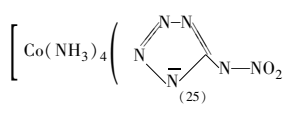
So this method allows to obtain compound (23) with a higher yield during a shorter period of time.

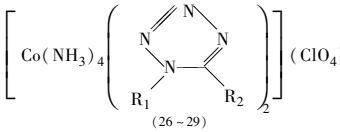
To investigate the properties of others tetraaminates of cobalt(Ⅲ) complexes, perchlorates of 5-substituted and 1, 5-disubstituted tetrazoles were synthesized (Table 2).

Table 2　Characteristics of tetraamminates of cobalt(Ⅲ)

Entry	R, R^1, R^2	$T_{decomp.}$/℃	E_a/kJ · mol^{-1}	$\rho_{calc.}$/g · cm^{-3}	$D_{\rho calc.}$/km · s^{-1}
23	R = NO_2	234	212.2	1.97	8.1
24	R = CH_3	252	204.7	1.75	6.8
25	R = H	239	228.6	1.86	6.9
26		238	231.6	1.90	7.1
27	R^1 = H, R^2 = NH_2	238	293.6	–	–
28	R^1 = R^2 = NH_2	233	204.6	1.85	7.3
29	R^1 = CH_3, R^2 = NH_2	234	218.3	1.79	7.5


(23 ~ 24)


(25)


(26 ~ 29)

The test for the minimum charge in blasting cap 8# showed that all of the above complexes possess initiating ability.

The minimum charge of these compounds for RDX decreases in the sequence:

(27) ≈ (25) ≈ (26) > (28) ≈ (24) > (29) > (23).

Also, compound (26), (23), (27), (28) have certain sensitivity to laser impulse (pulse time ~2 ms, E ~1.5 J, λ ~1.06 μm, diameter of ray ~0.5 mm).

Laser initiation is a new method of activating the

charges of EC. This method ensures high safety of explosive works because it provides the high level of isolation of the light detonator from error impulses.

Light detonators are non-susceptible to electromagnetic impulses and impulses of static electricity.

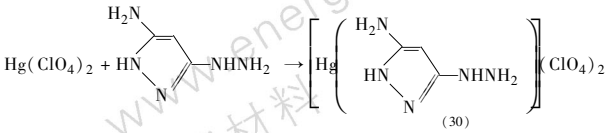
Laser initiation can be introduced in many explosive technologies which require individual approach in developing explosive systems:

(1) explosive welding, stamping, compacting, synthesis of new materials; (2) explosive mining works, dangerous in respect to gas and dust; (3) automated technologies with a pulsed periodic input of materials; (4) explosive technologies of a single action used for example, in the system of pyroautomatics of space shuttles or in protection systems for dangerous technological processes; (5) explosive technologies used in perforation of deep bore-holes; (6) technologies of extreme operating conditions using high electromagnetic fields.

Light blasting caps or film charges of light sensitive EC can be used for such technologies initiation of these charges may be effected by impulse laser through optical fiber (light guide) or directly in air.

Complex perchlorates of hydrazinoazoles can be used as a novel class of compounds possessing high sensitivity to laser impulse. This suggestion is based on the properties of hydrazinoazoles i. e. the azole ring is featured by high positive enthalpy of formation besides, the hydrazine fragment has low ionization potential. This supposition has been experimentally tried.

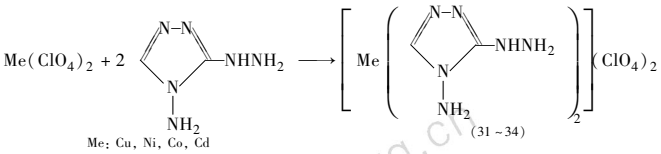
As a model compound, mercury (Ⅱ) perchlorate with 3-hydrazino-5-aminopyrazole as a ligand was synthesized:



(30)

Salt (30) showed high sensitivity to laser pulse (pulse time ~30 ns, initiation energy of threshold about 2.8×10^{-4} J).

Basing onto those results, we synthesized a range of complexes of d-metals using 3(5)-hydrazino-4-amino-1, 2,4-triazole as ligand:

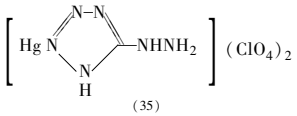


Me: Cu, Ni, Co, Cd

(31~34)

Complexes (31~34) also showed high sensitivity to laser pulse. Moreover, initiation thresholds were shown in our experiments to increase in the sequence: Cu < Cd < Ni < Co (the copper salt is the most - light sensitive compound). Which is identical to the row of oxidative ability of central ions characterized by the sum of ionization potentionals of cation and anion ($I_1 + I_2$). It means that the first stage of the laser initiation of perchlorate complexes of 3(5)-hydrazino-4-amino-1,2,4-triazole is the oxidation of ClO_4^- to ClO_4^* by d-metal ions, ClO_4^*-radical being the species that destruct and oxidize the ligands.

At last, 5-hydrazinotetrazole was taken as a ligand of choice. According to reaction, its mercury(Ⅱ) perchlorate complex was obtained:



(35)

This complex demonstrated the highest sensitivity to laser pulse with an extremly low initiation threshold (pulse-time ~30 ns, $E \sim 1 \times 10^{-4}$ J).

Depending on particular tasks, varions energetic metal complexes with differing values of initiation the resholds to laser Q-switch pulse (puls-time 10^{-8} s) or a non-Q-switch pulse (pulse-time 10^{-3} s) have been suggested. So, in the system of piroautomatics of rocket complexes in USA are successfuly used blasting caps using light-sensitive charges of BNCP.

For the perforators used in oil-gas wells in Russia, a system of laser initiation of cumulative charges was elaborated. The main light-sensitive elements of this system were complex perchlorates of hydrazinoazoles. Practical application of the explosion energy for studying the development of deformations in materials, constructions or the processes of initiation of primary explosive charges necessitates generation of detonation waves whose front would have a strictly specified shape. The existing methods for obtaining plane detonation waves require intricate experimental equipment and don't allow to simultaneously load

large areas. Even more complicated is the problem of creating cylindrical and spherical converging detonation waves.

A common shortcoming of the conventional means of initiation such as blasting caps or detonation cords is that they excite detonation in the main explosive charge only locally, at places of their location. These shortcomings can be eliminated by using a capless initiation method based on laser ignition of explosives. This method makes it possible to obtain a smooth front of profiled detonation waves on a surface of irregular shape. The method consists in that a film charge of an explosive highly sensitive to laser pulse is deposited onto the surface of a material to be loaded or on the main explosive charge. The film charge is exposed to a laser beam with energy density exceeding the critical value of the ignition threshold. The profile of the detonation wave is set by the shape of the initiated surface of the light-sensitive explosive.

The proposed method enables formation of any detonation wave profiles without additional explosive charges. An important advantage of the method is that the geometry of the laser beam can be easily controlled (expanded, deflected, narrowed) and automation is possible. In all cases the explosive is exploded remotely, with no essential limitations on the distance from which initiation is done.

The capless laser initiation has been successfully applied to study the possibility of hardening of steel surfaces by a plane shock wave formed by products appearing in a explosion of film charges of light-sensitive explosives. The strength of sample surface was improved as a result of loading by approximately 40% ~50%.

Consequently, energetic metal complexes are the perspective class of EC for the development of safety initiation systems and elaborating new laser technologies of blasting.

Acknowledgments

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用于起爆系统的无机炸药——配位络合物

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摘要: 介绍了含多氮杂环配位体的过氯酸盐系列络合物的合成研究。主要对新合成的化合物进行了性能研究及在安全电雷管和激光雷管的应用研究。

关键词: 无机化学; 络合物; 无机炸药; 起爆系统; 激光

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