Coordination explosives

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About seventy years ago, for average chemist explosives were associated with nitro-compounds or nitrates of alcohols called nitro-esters. Explosive individuals like azides or fulminates were not interchangeably called explosives, but were treated like explosive materials and used like primary explosives in detonating or igniting cups [1].

The potential possibility of usage of complexes as a modern explosives was noticed and developed about sixty years ago.

Obtained then, first far-reaching explosives with structure of transition metal complexes were characterized by too large sensibility to mechanical stimuli and these works were stopped [2].

Development of works at this kind of compounds was observed in the eighties of the twentieth century, when people started to search for new, low sensitive primary explosives not including toxic elements, like mercury or lead [3].

Researches lead to the first conclusion, that the best detonation characteristics have complexes of metals like: silver, cadmium, cobalt, copper, chromium, nickel and zinc, which have in their own structure oxidizing anion like: $N(NO_2)^-$, $NCIO_3^{-2}$, $C(NO_2)_3^-$, CIO_4^- , CIO_3^- , IO_4^- ,

One of the first representative of this kind of compounds was cis-bis-(5-nitrotetrazolato- N^2)tetraminecobalt(III) perchlorate, called BNCP (Fig. 1.).

Fig. 1. Structure of BNCP

$$\begin{bmatrix} H_{2}N & & & & \\ H_{2}N & & & \\ H_{2}N & & & & \\ H_{2}N & & & \\ H$$

Fig. 2. Structures of NHN and CoHN.

This compound, like all primary explosives, has short time transition from burning to detonation, thanks to this it can be applied as a primary charge in a detonation cup.

Its detonation characteristics, for example, its detonation velocity (carry out 9100 m/s do pressing density $1,97 \text{ g/cm}^3$) allows to apply this compound as a secondary explosive [4].

Simpler representative of complex primary explosives turned out to be tris(hydrazine)nickel(II) nitrate(V) (NHN), described in article [5] or its analogue including cobalt as a central atom (CoHN) (Fig. 2.).

Mentioned compounds did not find broad application in the branch of detonation cups and detonators, due to relatively low detonation parameters, what determined the use of their large amounts.

Crucial parameter of coordination explosives turned out to be their sensitivity to the laser light. Russian scientists started works on the series of compounds having the structure of perchloric complexes of metals with tetrazol derivatives.

Obtained compounds, detonated, when initiated by the laser light at wave length 800 nm and energy 0,5 mJ [6].

Cudziło and Szmigielski [7] from Military University of Technology studied ability to detonation process, under the influence of laser light at wave length 1,06 μ m and energy density on the level of 50 mJ/cm², of perchloric complexes of nickel, silver and copper containing as a ligand 4-amino-5(3)-hydrazine-1,2,4-triazole (HAT).

Researches showed, that obtained compounds presented relatively low sensitivity to mechanical stimuli, such as friction (8-10 N) and were able to initiate crystal of pentrite

Complexes of transition metals initiated by laser light can be applied as an igniting materials, as well as in electrical detonators and also in the artillery tube of the ammo or rocket engines.

Mixture of bis(1,2-ethylenodiamine)copper(II) perchlorate with polymer binder, such as polybutadiene terminated by hydroxyl groups or popular high-energetic polimer GAP (poly(glycidyl azide)) burns | illuminated by laser impulse with length 860 nm and power 0,3 W [8, 9].

This compound shows relatively high detonation parameters, which were described in article [10] and are characterized by relative ability to perform work in the underwater detonation test at the level of 110 % of trotyl (TNT) value and about 75 % of pentrite (PETN), hexogen (RDX) and octogen (HMX) values.

$$\begin{array}{c|c} & \text{CH}_2 & \text{CH}_2 \\ & \text{H}_2 \text{N} & \text{NH}_2 \\ & \text{H}_2 \text{N} & \text{NH}_2 \\ & \text{CH}_2 & \text{CH}_2 \end{array} \\ (\text{CIO}_4)_2$$

Fig. 3. Structure of bis(1,2-etylenodiamine)copper(II) chlorate(VII).

Similar parameters show other analogue nitrate and perchlorate chelating complexes of hydrazine (N_2H_4) and 1,2-ethylenodiamine (EN) with such metals like: copper, cobalt, nickel, mercury, cadmium, chromium and zinc.

The newest trend in the branch of detonation cups and detonators is the conception called NPD or NPED, it is Non Primary Explosive Detonator – detonator without primary explosive. Classical detonation cup is composed of two-part filling, primary explosive on the top – commonly lead azide, and the layer of pressed secondary explosive on the bottom of a cup.

NPED conception assumes elimination of primary explosive charge and its replacement by pyrotechnic mixture able to detonation and ignition of pentrite to detonation, or total filling of cup with mixture of compounds or compound able to detonation, but with a high usage safety – low sensitivity to friction, impact and electrostatic spark.

Conception of this type of detonators presented NITRO NOBEL company in the patent description [11].

Transition metals coordination compounds with ligands reach in nitrogen are often characterized by the ability to short time transition from burning to detonation and low sensitivity for mechanical

Table I

Percentage of tested compounds maximum pressure with respect to classical explosives determined by underwater detonation test

| Tested explosive | P _{max} | | | |
|---|------------------|-------|------|-------|
| | %RDX | %TNT | %HMX | %PETN |
| $[Cu(EN)_2](CIO_4)_2$ | 85,2 | 107,1 | 86,2 | 84,8 |
| [Co(EN) ₃](CIO ₄) ₃ | 77,4 | 97,2 | 78,3 | 77,0 |
| $[Ni(EN)_3](CIO_4)_2$ | 72,8 | 91,5 | 73,7 | 72,5 |
| $[Hg(EN)_2](CIO_4)_2$ | 80,2 | 100,8 | 81,1 | 79,8 |
| $[\operatorname{Cd}(N_2H_4)_3](\operatorname{CIO_4})_2$ | 72,2 | 90,7 | 73,0 | 71,8 |
| $[\operatorname{Cr}(N_2H_4)_3](\operatorname{CIO_4})_3$ | 83,5 | 104,9 | 84,4 | 83,1 |
| $[Cd(N_2H_4)_3](NO_3)_2$ | 74,5 | 93,6 | 75,3 | 74,1 |
| $[Zn(N_2H_4)_3](NO_3)_2$ | 69,2 | 86,9 | 70,0 | 68,8 |
| $[Co(N_2H_4)_3](NO_3)_3$ | 73,6 | 92,6 | 74,5 | 73,3 |
| $[Ni(N_2H_4)_3](NO_3)_2$ | 83,6 | 105,0 | 84,5 | 83,1 |

or electrostatic stimuli. It can have effects in the development of the conception of detonators NPED with this type of coordination compounds filling.

Designing of explosives ignited by laser light, can contribute in the introduction to the world market of safe detonators and detonation cups, significantly improving standards of work, as well as decreasing ability of illegally acquired agents for terrorist attack application.

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