



## **Study of the Interaction of Polynitro Compounds with Transition Metals Coordination Complexes with 1,5-Pentamethylenetetrazole as a Ligand**

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**Abstract:** Perchlorate complexes of d-metals with tetrazole-containing ligands are proposed for application both as explosives for safe initiation systems and as modifiers of burning rate for propellants. However, the problem of compatibility of organic polynitro compounds with the complexes has not yet been solved. In the present article the results of investigation of the influence of perchlorate complexes of cobalt, copper and nickel with 1,5-pentamethylenetetrazole as a ligand on thermal decomposition of energetic materials ranging from 1,1-diamino-2,2-dinitroethylene (FOX-7), to cyclic cyclotetramethylenetetranitroamine (HMX) and caged hexanitrohexaazawurtzitane (CL-20) have been reported. Thermal stability of the individual compounds and their mixtures with coordination complexes has been assessed on the basis of differential thermal analysis and the study of ignition temperatures after 5-second delay. The fraction of the complexes in the formulations with polynitro compounds amounted to ~10%.

**Keywords:** Chemical compatibility, 1,5-pentamethylenetetrazole, perchlorate complexes of d-metals, organic polynitro compounds, FOX-7, HMX, CL-20, thermal decomposition, burning rate, test

### **Introduction**

Researchers in many countries pay great attention to elaboration of novel

tests of chemical compatibility of energetic compounds with contacting materials. For example, DSC, DTA and TGA methods were suggested for testing chemical compatibility of inorganic primary explosives such as energetic salts with a short deflagration-to-detonation transition distance [1].

To test the compatibility, the temperatures of the onset of decomposition ( $T_{sd}$ ) of individual energetic compounds (EC) and their mechanical mixtures with contacting materials, determined by DSC technique, were recommended for use according to NATO Standardization Agreement STANAG 4147.

Test criteria of compatibility are based on the shift of the thermal decomposition peak (the onset of thermal decomposition temperature) for the tested mixture of compounds against the same parameters for individual EC used in the tested mixture. If the temperature of thermal decomposition of the mixture differs from that of individual components not more than by 0-4 °C, both materials comprising this mixture are regarded as mutually compatible.

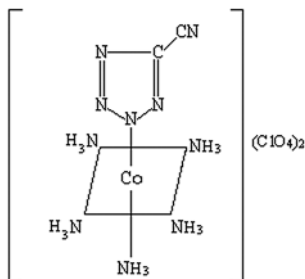
When the temperature of thermal decomposition of the above mixture is lower than that of its individual ingredients by 4-20 °C, the compatibility of materials forming the mixture is uncertain. When the lowering of temperature of thermal decomposition of the tested mixture exceeds 20 °C compared to that of individual components, the ingredients of the mixture are regarded incompatible and obviously interact with each other.

DTA analysis was also used by Chinese researchers for testing compatibility of primary explosives with contacting materials. According to Chinese sources, when DTA exothermic peak for the tested mixture consisting of an explosive and a contacting material shifts towards lower temperatures in comparison with the peak of an individual explosive by 0-2 °C, or 3-5 °C, or 6-15 °C, or more than 15 °C, the tested materials are regarded as compatible, having a minor incompatibility, incompatible, or dangerously incompatible, correspondingly.

From comparison of the presented assessment criteria of materials compatibility by means of DSC and DTA techniques, it appears that the more strict criteria of compatibility are reported in Chinese sources rather than in STANAG 4147.

Perchlorate complexes of d-metals with nitrogen heterocycles as ligands have been used as explosives in safety initiation systems and as modifiers of burning rates of propellants [2, 3]. But the problem of compatibility of perchlorate metal complexes with organic polynitro compounds has not been solved. Only several pentaamminecobalt (III) perchlorate complexes with tetrazole ligands were investigated with respect to compatibility with HMX and some other organic compounds [4]. American researchers [5] have studied the compatibility of HMX with [2-(5-cyanotetrazolato- $N^2$ )]pentaamminecobalt (III) perchlorate (explosive

CP) which is used in USA in safety blasting caps.



[2-(5-Cyanotetrazolato-N<sup>2</sup>)]pentaamminecobalt (III) perchlorate  
(explosive CP)

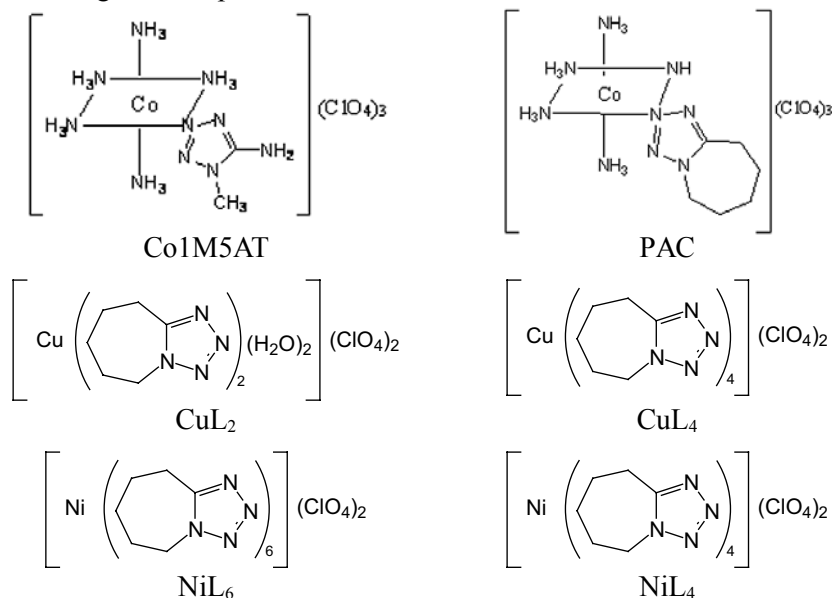
They showed that the temperature of the onset of decomposition of mechanical mixtures of HMX and CP decreased by  $\sim 20$  °C in comparison with the onset temperature of individual HMX. Consequently, HMX and CP were regarded as partly compatible according to recommendations of standard STANAG 4147. A mechanical mixture of HMX and CP had a lower value of the activation energy of thermal decomposition as compared to the individual polynitroamine, and its decomposition rate at high temperatures was 3-5 times higher than in pure HMX. However, the mechanical mixture of HMX and CP could be kept for more than 20 years at room temperature without any changes that made commercial use of CP in blasting caps quite possible. Hence, the recommendations of standard STANAG 4147 were useful for the estimation of compatibility of HMX and CP and could be used as a test of compatibility of perchlorate metal complexes with organic polynitro compounds.

We tried to estimate experimentally the compatibility of an aliphatic polynitro compound, 1,1-diamino-2,2-dinitroethylene (FOX-7), a cyclic nitramine, cyclotetramethylenetetranitramine (HMX), a caged hexanitrohexaazaisowurtzitane (CL-20) with some model perchlorate metal complexes. Both recording the ignition temperatures under 5-second delay and differential thermal analysis (DTA/DTG) were used for testing individual compounds and mechanical mixtures of polynitro compounds with perchlorate metal complexes.

## Materials and Methods

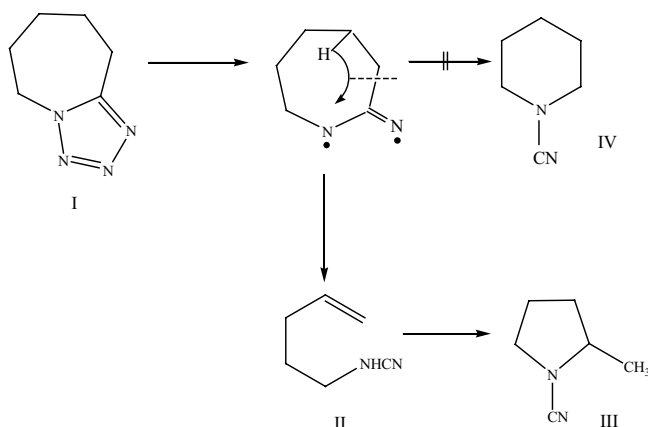
We investigated the compatibility of organic polynitro compounds with CP analogs – (1-methyl-5-aminotetrazole-N<sup>2</sup>)pentaamine cobalt (III) perchlorate

(Co1M5AT) and (1,5-pentamethylenetetrazole- $N^3$ ) pentaammine cobalt (III) perchlorate (PAC), as well as perchlorate complexes of copper and nickel with pentamethylenetetrazole (PMT, L, I) as a ligand [4, 6]. Chemical structures of the investigated complexes are shown in Scheme 1.



**Scheme 1. Perchlorate metal complexes:** Co1M5AT – (1-methyl-5-aminotetrazole – $N^2$ )pentaamminecobalt(III) perchlorate; PAC – (1,5-pentamethylenetetrazole- $N^3$ ) pentaamminecobalt(III) perchlorate; CuL<sub>2</sub> – di-aqua-bis-(1,5-pentamethylenetetrazole) copper(II) perchlorate; CuL<sub>4</sub> – tetra(1,5-pentamethylenetetrazole) copper(II) perchlorate; NiL<sub>6</sub> – hexa(1,5-pentamethylenetetrazole) nickel(II) perchlorate; NiL<sub>4</sub> – tetra(1,5-pentamethylenetetrazole) nickel(II) perchlorate.

PMT, being used as a ligand, is known to decompose in several steps in vacuum in the temperature range of 450–675 °C. On the first step the tetrazole ring of PMT (I) is destroyed and the nitrogen molecule is evolved. The next steps lead to acyl-4-en-cyanamid (II) and 1-cyano-2-methylpyrrolidine (III). Probably, compound (II) is formed from a nitrene intermediate as is shown in Scheme 2 [7].



**Scheme 2.** Thermal decomposition of PMT.

The choice of model perchlorate metal complexes with PMT as a ligand which were studied in compatibility tests with organic polynitro compounds was based on the fact that perchlorates CoIM5AT and PAC have short deflagration-to-detonation transition distances and formerly were investigated in model blasting caps [6, 8], whereas perchlorate complexes of copper and nickel were used as modifiers of burning rates of model propellants [9, 10]. Consequently, the coordination compounds studied in the present work have been really in contact with organic polynitro compounds.

The complex salts were prepared by mixing perchlorates of d-metals with PMT in dilute aqueous perchloric acid solutions. Reactions were carried out at 20-30 °C. The reactions proceeded for several hours. A small excess of the ligand (5-50%) over the stoichiometric quantity was used. The precipitated metal complexes were filtered off, washed with ethanol and dried in a vacuum thermostat. Structures of the perchlorate complexes were confirmed by C, H, N – analysis (analyzer Hewlett-Packard 185B), IR- and NMR <sup>1</sup>H-spectroscopy (Shimadzu FTIR-8400 and Bruker AC-200, respectively). The UV-spectra of cobalt (III) perchlorates (Shimadzu UV-2401PC) showed that they had octahedral structures with CoN<sub>6</sub> as chromophors. Differential thermal analysis (derivatograph Paulic, Paulic, Erdei Model Q-1500D (MOM, Hungary)) was used to study the thermal decomposition of the energetic materials. The rates of samples heating amounted to 5 K/min.

Burning rates of energetic materials were measured in a constant pressure bomb BCP-400 (this part of investigations was made in collaboration with Professor V.P. Sinditskii and his co-workers in D.I. Mendeleev Russian Chemical-Technological University, Moscow) [12].

## Results and Discussion

### Thermal decomposition of perchlorate complexes

The results of TG/DTA experiments showed that PMT ligands in perchlorate complexes were oxidized by  $\text{ClO}_4^-$  anions and central ions in several steps. Temperatures of the onset of intense decompositions ( $T_{\text{bid.}}$ ) for the last decomposition step of the complexes are shown in Table 1.

**Table 1.** Temperatures of the onset of the intensive decompositions ( $T_{\text{bid.}}$ ) for the last decomposition steps of the complexes studied [13]

Complex	Index	$T_{\text{bid.}}$ [°C]
$\text{Cu(PMT)}_4(\text{ClO}_4)_2$	$\text{CuL}_4$	258
$\text{Cu(PMT)}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{CuL}_2$	235
$\text{Ni(PMT)}_6(\text{ClO}_4)_2$	$\text{NiL}_6$	255
$\text{Ni(PMT)}_4(\text{ClO}_4)_2$	$\text{NiL}_4$	235
$[\text{Co}(\text{NH}_3)_5\text{PMT}](\text{ClO}_4)_3$	PAC	250
$[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CN}_4\text{NH}_2)](\text{ClO}_4)_3$	$\text{Co1M5AT}$	260

TG analysis showed that the mass of the complex  $\text{CuL}_4$  decreased by ~30% with an exo-effect under heating from 175 to 240 °C. Probably, one PMT ligand molecule was oxidized by one perchlorate anion in the first step of the complex decomposition. The second molecule of PMT ligand was oxidized by the last perchlorate anion of the outer sphere at temperatures from 240 °C to 305 °C. The solid residue after decomposition was of unknown composition and contained copper.

The first thermal decomposition step of perchlorate complex  $\text{CuL}_2$  took place at temperatures 70-165 °C with a small exo-effect and mass loss of the sample about ~10%. Probably, at this step the elimination of two molecules of water takes place followed by the reorganization of the inner sphere of complex  $\text{CuL}_2$ . Then tetrazole rings of PMT ligand molecules were destroyed and the formed nitrenes were oxidized by external perchlorate anions. The temperature range of the second step of decomposition covers the interval from 171 °C to 317 °C. The mass loss of the sample at this step was about ~60%.

Perchlorate complex  $\text{NiL}_6$  undergoes the thermal decomposition in two steps. One PMT ligand molecule was oxidized by a perchlorate anion at the first step of thermal decomposition within the interval 150-225 °C. The mass loss of the sample at this step was ~22%. The first step of complex  $\text{NiL}_6$  decomposition was exothermal. Five nitrogen molecules evolved at the second step of decomposition resulted from degradation of PMT tetrazole rings at temperatures 295-460 °C.

Simultaneously two nitrene species were oxidized by an external perchlorate ion. The reactions taking place at the second step of  $\text{NiL}_6$  thermal decomposition were also exothermal. The mass loss of the sample on this step was  $\sim 42.3\%$ . The solid residues appeared to be the mixture of compounds of unknown composition.

The thermal decomposition of perchlorate complex  $\text{NiL}_4$  proceeded in two exothermal steps. Two PMT ligand molecules were oxidized by one external perchlorate anion at temperatures 230-290 °C on the first step of decomposition accompanied by mass loss of the sample  $\sim 46.4\%$ . The third PMT ligand molecule was oxidized by the last perchlorate anion on the second decomposition step in the temperature range 320-440 °C. The mass loss of the sample on this step was  $\sim 29.3\%$ . The solid residue after the sample decomposition was apparently the mixture of compounds of unknown composition (mass of the residue comprised ca. 25% of the initial sample mass).

For all of the studied mixed ligands ammine complexes of cobalt (III) the first step of decomposition was the evolution of ammonia molecules from their inner sphere. These processes resulted in the rearrangement of the inner sphere and decomposition of the ligands. Further one or more steps of decomposition and oxidation of the residual ligands (ammonia and PMT) by perchlorate anions took place. Evolution of four molecules of ammonia comprised the first step of complex PAC decomposition at temperatures from 95 °C to 245 °C. The reactions exhibited endothermal effects. The mass loss of the sample in these processes equals to  $\sim 14.7\%$ . Under further heating the sample of complex PAC melted at 245 °C and decomposed over the temperature range 250-350 °C with a large exothermal effect. The loss of the sample mass on this step of decomposition was  $\sim 71.1\%$ . The final solid residue apparently consisted of cobalt (III) oxide  $\text{Co}_2\text{O}_3$  ( $\sim 14.1\%$  of the sample mass). This oxide usually was formed as a result of perchlorate Co (III) complexes decompositions in air. The thermogram of cobalt (III) complex  $\text{Co1M5AT}$  decomposition showed two exothermic steps with the temperatures of the onset of the intensive decomposition at 216 °C and 238 °C.

### **Ignition temperatures of polynitro compounds and their mixtures with PMT perchlorate complexes**

In Table 2 are presented the results of the study of ignition temperatures at a 5-second delay of organic polynitro compounds and their mechanical mixtures with perchlorate complexes of d-metals. The temperatures of ignition were determined by the Wood's melted bath technique.

**Table 2.** Ignition temperatures of the studied explosives and their mixtures with coordination complexes at a 5-second delay

HMX and its mixtures	Ignition temperatures, [°C]	CL-20 and its mixtures	Ignition temperatures, [°C]	FOX-7 and its mixtures	Ignition temperatures, [°C]
HMX	287	CL-20	220	FOX-7	284
HMX + NiL <sub>6</sub>	282.5	CL-20 + NiL <sub>6</sub>	223.5	FOX-7 + NiL <sub>6</sub>	287
HMX + NiL <sub>4</sub>	290.5	CL-20 + NiL <sub>4</sub>	216	FOX -7 + NiL <sub>4</sub>	287
HMX + CuL <sub>4</sub>	291.5	CL-20 + CuL <sub>4</sub>	222.5	FOX -7 + CuL <sub>4</sub>	276.5
HMX + Co1M5AT	246	CL-20 + Co1M5AT	227.5	FOX-7 + Co1M5AT	247
HMX + PAC	280.5	CL-20 + PAC	224.5	FOX -7 + PAC	257
HMX + CuL <sub>2</sub>	280	CL-20 + CuL <sub>2</sub>	212	FOX-7 + CuL <sub>2</sub>	282.5

Analyzing the observed values of ignition temperatures of the individual energetic compounds and their mixtures with coordination complexes, according to the recommendations of STANAG 4147, the following preliminary conclusions can be drawn.

- HMX is completely compatible with NiL<sub>6</sub> and CuL<sub>4</sub> complexes; apparently there exists a negligible interaction with NiL<sub>4</sub>, CuL<sub>2</sub> and PAC (the ignition temperature is reduced by 4-7 °C), and is incompatible with complex Co1M5AT (decrease in the ignition temperature by 41 °C).
- CL-20 is completely compatible with NiL<sub>6</sub>, CuL<sub>4</sub>, Co1M5AT and PAC, apparently compatible with NiL<sub>4</sub> (the ignition temperature is decreased by 4 °C), and a minor incompatibility occurs with CuL<sub>2</sub> (decrease in the ignition temperature by 8 °C),
- FOX-7 is compatible with perchlorates NiL<sub>6</sub>, NiL<sub>4</sub> and CuL<sub>2</sub>, partially compatible with CuL<sub>4</sub> (the ignition temperature is reduced by 8 °C) and incompatible with CP analogs, namely, compound PAC (lowering the ignition temperature by 27 °C) and complex Co1M5AT (decrease in the ignition temperature as much as 37 °C).

### Differential thermal analysis of polynitro compounds and their mixtures with PMT perchlorate complexes

DTA was used for more precise investigations of compatibility of the organic polynitro compounds with some PMT complexes which are rather reactive under conditions of the ignition temperatures analysis. Table 3 shows both the temperatures of the onset of decomposition at the first low-temperature step for the studied polynitro compounds and their mixtures with PMT perchlorate complexes ( $T_{b,d}$ , °C), and the temperatures of intensive decomposition at high-



temperature steps for the same compounds and their mechanical mixtures with PMT complexes ( $T_{b.i.d.}$  °C).

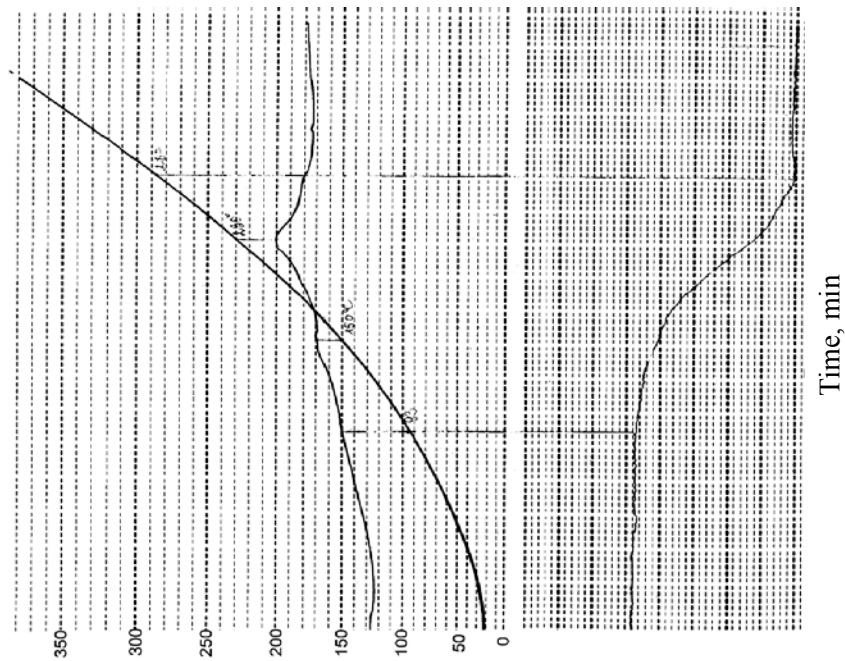
**Table 3.** Values of  $T_{b.d.}$  °C and  $T_{b.i.d.}$  °C of polynitro compounds and their mechanical mixtures with PMT perchlorate complexes

Polynitro compounds studied and their mixtures with PMT complexes	$T_{b.d.}$ °C	$T_{b.i.d.}$ °C
HMX	275	290
HMX+PAC	216	280
HMX+CuL <sub>2</sub>	93	230
CL-20	220	239
CL-20+NiL <sub>4</sub>	210	237
FOX-7	206	270
FOX-7+CuL <sub>4</sub>	193	260
FOX-7+PAC	208	257
FOX-7+Co1M5AT	210	241

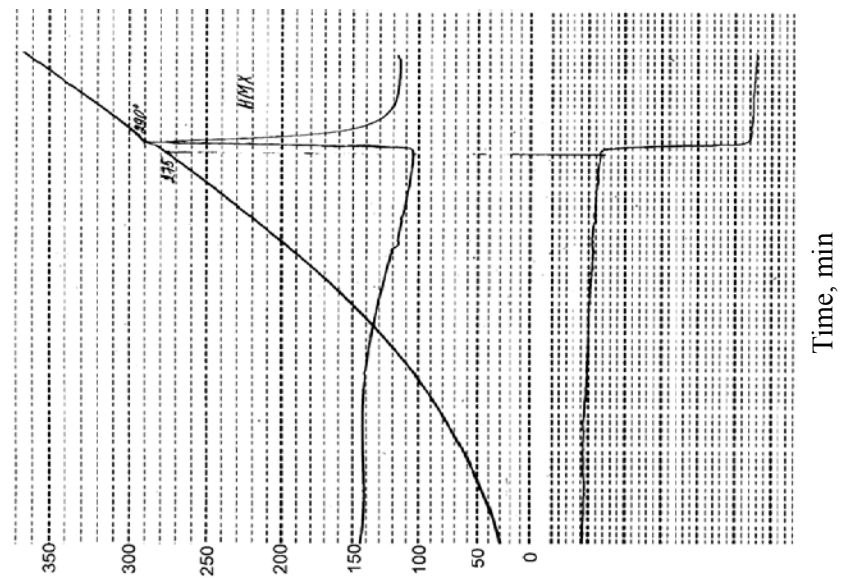
Differential thermal analysis data demonstrated that addition of 10% perchlorate complex PAC to HMX changed the nature of its thermal decomposition. Thermal decomposition of the mixture became a two-step process instead of an one-step decomposition of the polynitramine.  $T_{b.d.}$  decreased from 275 °C to 216 °C. Consequently, compounds PAC and HMX are entirely incompatible. Intensive chemical interactions very likely took part in the mixture at high temperatures. Decomposition of the mixture of HMX with 10% CuL<sub>2</sub> complex began at ~90 °C and finished at ~290 °C.  $T_{b.i.d.}$  decreased from ~290 °C to ~230 °C. Apparently intensive chemical interactions between the polynitramine and complex CuL<sub>2</sub> or products of their thermal decomposition also took place in this mixture at high temperatures (Figures 1 and 2)

The pattern of thermal decomposition of the mechanical mixture of CL-20 and NiL<sub>4</sub> was similar to that of the individual polynitramine. The value of  $T_{b.d.}$  of the mixture was reduced by 10 °C compared to the  $T_{b.d.}$  of individual CL-20. Consequently, polynitramine CL-20 and complex NiL<sub>4</sub> have limited compatibility.

Presence of the complexes exerted a pronounced effect on the decomposition reactions of FOX-7 at every step. Mechanical mixtures of FOX-7 and perchlorate complex 1M5AT decomposed in one exothermal step, whereas mixtures of FOX-7 with perchlorate complexes CuL<sub>4</sub> and PAC exhibited two steps of thermal decomposition. Mechanical mixtures of FOX-7 with perchlorate complex CuL<sub>4</sub> had  $T_{b.d.}$  value lower by 13 °C than the individual nitro compound. Very likely, this



**Figure 2.** DTA/TG curves of decomposition of the mixture HMX + CuL<sub>2</sub>.



**Figure 1.** DTA/TG curves of HMX decomposition.

nitro compound was only partly compatible with the complex. Both mechanical mixtures of FOX-7 with perchlorate ammine complexes PAC and 1M5AT and the individual nitro compound had the same values of  $T_{b,d}$ . So, these energetic compounds demonstrated full compatibility according to recommendations of NATO Standardization Agreement STANAG 4147. The values of  $T_{b,i,d}$  of high-temperature decomposition steps of mechanical mixtures of FOX-7 with the studied coordination complexes were lower (by  $\sim 13$  °C for perchlorate complex PAC and by  $\sim 29$  °C for perchlorate complex 1M5AT) compared to  $T_{b,i,d}$  of high-temperature decomposition step of individual FOX-7. Supposedly the decomposition products of the perchlorates of ammine cobalt complexes reacted with the products of decomposition of the nitro compound and catalyzed the decomposition of FOX-7 at high temperatures. Very likely, these energetic perchlorate complexes would catalyze the burning of FOX-7.

So, the results of DTA confirmed and defined the data of the study of the ignition temperatures of individual nitro compounds and their mechanical mixtures with PMT perchlorate complexes.

Consequently, the measurements of the ignition temperatures at 5-second delay experimentally proved to be useful as a test for a preliminary assessment of the compatibility of organic energetic compounds with complex d-metal perchlorates.

### Burning rates of the formulation HMX + CuL<sub>2</sub>

We suggested that metal complexes which lowered  $T_{b,i,d}$  values and ignition temperatures at 5-second delay would be able to catalyze the burning rate of a given nitro compound. This suggestion was experimentally checked on the charges of mechanical mixtures consisting of 95% HMX and 5% CuL<sub>2</sub>. The charges were pressed in polymer tubes under pressure 1500 kg/cm<sup>2</sup>. Dependence of burning rates of the mixture HMX + CuL<sub>2</sub> on pressure is shown in Table 4 and Figure 3.

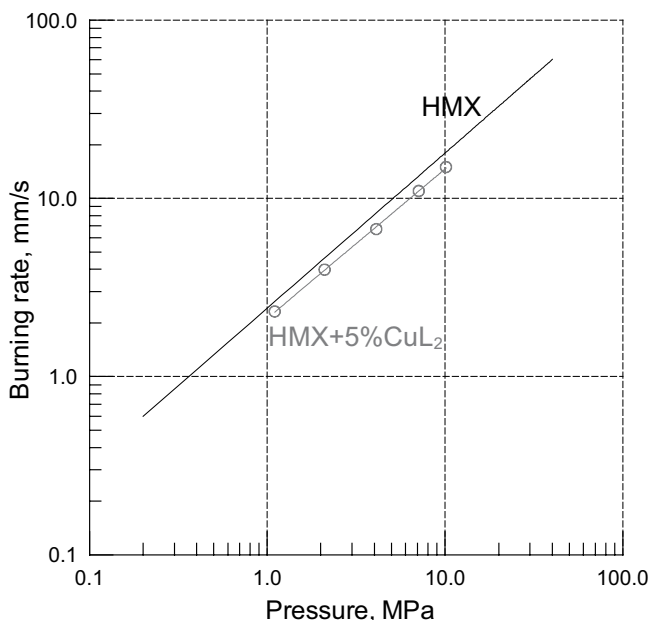
**Table 4.** Dependence of burning rates of the mixture HMX + CuL<sub>2</sub> on pressure

№	Pressure, MPa	Burning rate, mm/s
1	10.1	15
2	7.1	11
3	4.1	6.72
4	2.1	3.98
5	1.1	2.32

Figure 3 showed that complex CuL<sub>2</sub> was an essentially inert additive which

lowered the HMX burning rate only by 5% without changing the exponent value in the law of burning. Consequently, perchlorate complex  $\text{CuL}_2$  exhibited no catalytic activity in the process of HMX combustion.

So we may conclude that the results of DTA studies and the estimation of the ignition temperatures of nitro compounds FOX-7, HMX and CL-20 and their mechanical mixtures with energetic perchlorate d-metal complexes could not be directly used for prediction of the perchlorate complexes catalytic properties in the processes of the polynitro compounds combustion.



**Figure 3.** Dependence of burning rates on pressure for individual HMX and a formulation HMX +  $\text{CuL}_2$ .

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## References

- [1] a) Miszczak M., Brzyski A., Milewski E., Goryca W., An Analysis of Test and Assessment Methods on Chemical Compatibility of Primary Explosives, *Proc. 11<sup>th</sup> Seminar "New Trends in Research of Energetic Materials"*, Pardubice, Czech Republic, 09-11 April **2008**. Part 1. pp. 246-253; b). Yan N., Sun W., Hua C., The Discussion of Primary Explosive Compatibility, *Theory and Practice of Energetic Materials*, (Wang Y., Huang P., Li S., Eds.), Interscience Press Beijing, New York, **2005**, vol. 6. pp. 327-331.
- [2] Danilov Yu.N., Ilyushin M.A., Tselinsky I.V., *Industrial Explosives. Part 1. Primary Explosives (Text-book)*. 2nd ed., SPbSIT(TU), Saint-Petersburg **2004** (in Rus.).
- [3] Ilyushin M.A., Tselinsky I.V., Sydarikov A.M., Preparation of Components for Energetic Materials, (Tselinsky I.V. Ed.), Leningrad State University named after A.S. Pushkin, Saint-Petersburg **2006** (in Rus.).
- [4] Ilyushin M.A., Gruzdev Yu.A., Bachurina I.V., Smirnov A.V., Tselinsky I.V., Andreeva Yu.N., The Compatibility of High Explosives with Energetic Coordination Complexes of Cobalt (III), *Proc. X Seminar "New Trends in Research of Energetic Materials"*, Pardubice, Czech Republic, 25-27 April **2007**, Part 2, pp. 640-645.
- [5] Burnham A.K., Weese R.K., Andrzejewski W.J., Kinetics of HMX and CP Decomposition and Their Extrapolation for Lifetime Assessment, *Proc. Int. Annual Conf. ICT 36<sup>th</sup>*, Karlsruhe **2005**, pp. 153-165.
- [6] Smirnov A.V., Ilyushin M.A., Tselinskii I.V., Synthesis of Cobalt (III) Ammine Complexes as Explosives for Safe Priming Charges, *Rus. J. Appl. Chem.*, **2004**, 77(5), 794-796.
- [7] Wentrup C., Nitrenes Derived from Polymethylenetetrazoles, *Tetrahedron*, **1971**, 27(6), 1281-1286.
- [8] Zhilin A.Yu., Ilyushin M.A., Tselinsky I.V., Nikitina Yu.A., Kozlov A.S., Shugalei I.V., Complex Energetic Perchlorates of Cobalt (III) Amminates with Cyclopentamethylenetetrazole as Ligand, *Rus. J. Appl. Chem.*, **2005**, 78(2), 188-192.
- [9] Ilyushin M.A., Tselinsky I.V., Bachurina I.V., Novoselova L.O., Konyushenko E.N., Kozlov A.S., Gruzdev Yu.A., Application of Energy Saturated Complex Perchlorates, *AIP Conf. Proc. Zababakhin Scientific talks-2005*, (Avrorin E.N., Simonenko V.A., Eds.), Snezhinsk, Russia, 5-10 September 2005, Melville, New York **2006**, 849, pp. 213-217.
- [10] Bachurina I.V., Ilyushin M.A., Tselinskii I.V., Gruzdev Yu.A., High-Energy Complex Copper (II) Perchlorate with 1,5-Pentamethylenetetrazole as Ligand, *Rus. J. Appl. Chem.*, **2007**, 80(10), 1643-1646.
- [11] a) Avanesov D.S., Manual on Physic-Chemical Tests of Explosives, State Publication House of Defense Literature, Moscow **1959**, (in Rus.). b) Loskutova L.A., Kozlov A.S., Ilyushin M.A., Bachurina I.V., Ignition Temperatures of Energetic Materials, *Methodic instruction*, SPbSIT(TU), Saint Petersburg **2007**, (in Rus.).
- [12] Ilyushin M.A., Tselinsky I.V., Bachurina I.V., Gruzdev Yu.A., Sinditskii V.P., Serushkin V.V., Egorshv V.Yu., Preparation, Properties and Application of

Energetic Complex Perchlorates of d-Metals, *Centr. Europ. J. Energ. Mater.*, **2006**, 3(4), 41-49.

- [13] Ilyushin M.A, Bachurina I.V., Smirnov A.V., Tselinsky I.V., Gruzdev Yu.A., About Compatibility of Metalcomplexes with Organic Energetic Compounds, *Conf. "Shock Waves in Condensed Matter"* Saint Petersburg, 23-26 November **2008**, pp. 78-82 (in Rus.).