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Preparation, Properties and Application of Energetic Complex Perchlorates of d-Metals*)

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Abstract: Methods for the synthesis of novel energetic complex perchlorates of d-metals have been developed. According to derivatographic analysis data, the complexes are thermally stable compounds. One of the promising ways of regulating ballistic characteristics of highly filled energetic formulations is the introduction of burn modifiers. Complex compounds of d-metals are known to be effective modifiers of the process of burning. Ballistic tests were made in a constant pressure bomb and demonstrated that the prepared compounds are promising modifiers of the burn rate and can be used in the developed formulations of rocket propellants.

Keywords: complex perchlorates, 1,5-pentamethylenetetrazole, modifiers of burning, derivatographic analysis, drop hammer test, ballistic test, bomb of constant pressure

Introduction

The report is devoted to the synthesis and characterization of coordination compounds in the series of perchlorates of d-metals containing substituted

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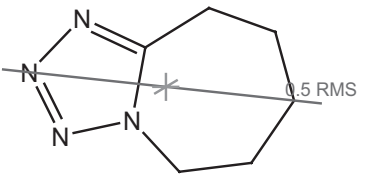
tetrazole as ligand. Considerable attention to this class of energetic materials is caused by their application in safe detonators and rocket propellants.

Discussion

Synthesis and properties of the perchlorate complexes

We have carried out the synthesis of new energetic d-metal complex perchlorates with 1,5-pentamethylenetetrazole (PMT) as ligand.



1,5-Pentamethylenetetrazole (PMT)

Preparation of metal complexes was performed according to the following reactions:

for Cu(II) complexes

$Cu(CH_3COO)_2 + n(CH_2)_5CN_4 + 2HClO_4 \rightarrow [Cu((CH_2)_5CN_4)_n](ClO_4)_2 + 2CH_3COOH$

n = 2, 4

for Co(III) complex

$[Co(NH_3)_5H_2O]^{3+}(ClO_4^-)_3 + PMT \rightarrow \{Co(NH_3)_5[PMT]\}^{3+}(ClO_4^-)_3 + H_2O$

The following compounds were prepared and investigated:

$Cu(PMT)_4(C1O_4)_2$ (**1**), $Co(NH_3)_5(PMT)(ClO_4)_3$ (**2**). The composition and structure of complexes **1** and **2** were supported by the results of elemental analyses; IR-, UV-, and NMR(H^1)-spectroscopy. The results of thermochemical studies of complex perchlorates by means of derivatographic method are presented in Tables 1 and 2.

Table 1. Derivatographic analysis of complex **1**

Products of thermal decomposition	ΔT °C	Effect	Residue, %	
			Found	Calculated
$[Cu(PMT)_4]\ (ClO_4)_2$	30-175	Endo	100	-
$Cu\ (PMT)_3\ (ClO_4)$	175-240	Exo	29.3	29.6
$Cu(PMT)_2$	240-305	Exo	29.3	29.6
CuC_xN_y	350→		40.9	

Table 2. Derivatographic analysis of complex **2**

Products of thermal decomposition	ΔT °C	Residue, %	
		Found	Calculated
$[Co(NH_3)_5(PMT)](ClO_4)_3$	60-245 (max 243)	100	
$Co(PMT)(ClO_4)_3$	245-360 (max 275, 295, 320)	85.0	85.3
$1/2Co_2O_3$	360-500	14.0	14.3

The data listed in Tables 1 and 2 show that complexes **1** and **2** are decomposed in several steps. Decomposition of the complexes begins when temperature rises above 200 °C. Removal of PMT molecule is the first step of decomposition of perchlorate complex **1.** For complex **2** during the first stage the process of inactivation and removal of NH_3 molecules from the inner sphere is observed. Subsequently the thermal decomposition of the tetrazole ligand occurs with the involvement of the perchlorate anion into oxidation reactions at the late stages of the complex destruction. According to the data of derivatographic analysis, the complexes are thermally stable compounds.

The drop hammer test of impact sensitivity according to GOST 4545-88 demonstrated that the sensitivity to impact of perchlorate complex **2** is similar to that of PETN. Sensitivity to impact of copper complex **1** was at the level of tetryl. Complex **2** has a crystal density near 1.82 g cm^{-3}. Sensitivity to impact of complex **2** (drop hammer K-44-II, mass of hammer 2 kg, H=25 cm, % of explosion) is 16% (the impact sensitivity of PETN is 12% under similar conditions). Complex **2** has a short distance of deflagration-to-detonation transition and can initiate charges of RDX in blasting cap No 8. Minimal charge of complex **2** for blasting RDX is near 0.4 g under this condition [1]**.** Detonation velocity of complex **2** at maximum density is near 6.98 mm μs^{-1}. (Detonation velocity calculated by method of A.A. Kotomin [2]). Consequently, complex **2** may serve as an initiating material with the detonation velocity close to that of TNT and sensitivity to mechanical stimuli like other modern high explosives. Perchlorate complex **1** does not initiate HE.

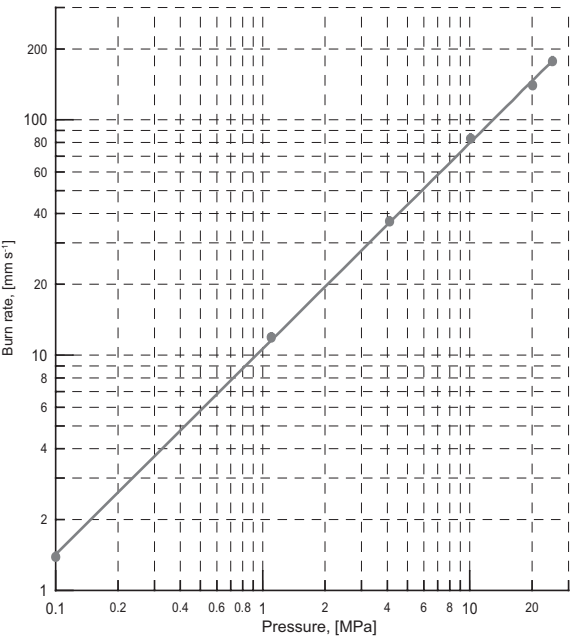


Figure 1. The rate of deflagration of complex **2** as a function of pressure.

The burn rates of perchlorate complexes **1** and **2** in the bomb of constant pressure (BCP – 400) were investigated. Charges of the perchlorate complexes were pressed into polymethylmethacrylate tubes with the internal and external diameters equal to 4 and 7 mm, respectively. Photoregister FR-14 was used for measuring the burn rates of complex **2.** Figure 1 demonstrates the rate of deflagration of complex **2.**

The pressure exponent in the equation for the burn rate of perchlorate complex **2** (ν) equals to 0.874. This value is a little lower than the pressure exponent in the equation for the burn rate of hexaammine cobalt (III) perchlorate ($[Co(NH_3)_6](ClO_4)_3$) (ν = 1) and aquapentaammine cobalt (III) perchlorate ($[Co(NH_3)_5(H_2O)](ClO_4)_3$) ($\nu$ = 1) which have the structures analogous to that of complex **2** [3]. It is noteworthy that perchlorate complex **2** burns partly in the condensed phase. This effect may be the result of the presence of CH_2- groups as a fuel in the ligand.

Complex **1** has a lower burn rate. Digital camera JVC GR-DVL 9800 was used to measure burn rates of complex **1.** Figure 2 shows the rate of deflagration of complex **1.**

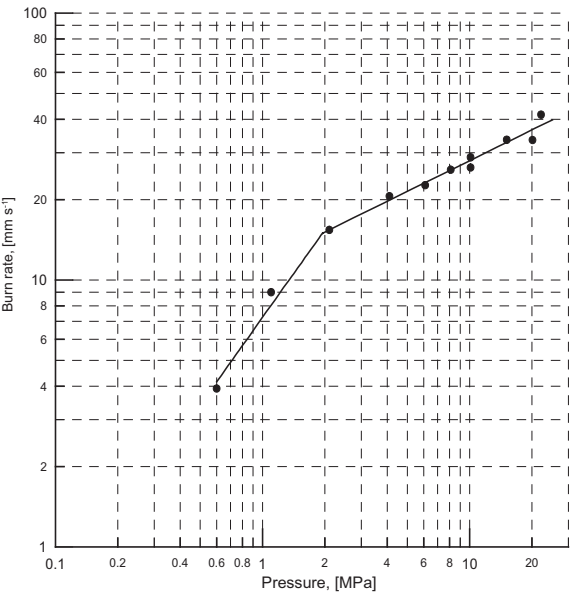


Figure 2. The rate of deflagration of complex **1** as a function of pressure.

The lower pressure limit of self-sustaining burning of perchlorate complex **1** is 0.5 MPa. In the interval from 0.5 MPa to 2 MPa the pressure exponent in the equation of burning (v) equals to 1.089 and shows that the process of burning takes place entirely in the gas phase. The line illustrating the dependence of the burn rate on pressure for values greater than 2 MPa changes the slope ($v = 0.383$) because of the change in the rate limiting stage. As the pressure rises, the processes in the condensed phase become dominant.

Experimental values of burn rate were used to calculate the burn temperatures and composition of burning products for complexes 1 and 2 at the studied pressures. The operation was carried out by means of REAL computer code. The code was developed by G.V. Belov for computer simulating of complex chemical reactions taking place at high temperatures and pressures.

The experimental formulae of perchlorate complexes ($Cu_1C_{24}H_{40}N_{16}Cl_2O_8$ (**1**) and $Co_1N_9H_{25}C_6Cl_3O_{12}$ (**2**)) and the values of enthalpies of formation (ΔH_f^0 = 439 kJ kg^{-1} for complex **1**, ΔH_f^0 = - 883 kJ kg^{-1} for complex **2)** were used to perform calculations. The calculated burn temperatures and composition of burning products of the perchlorate complexes at pressure 10 MPa are shown in Tables 3-5.

Table 3. The calculated burn temperatures for perchlorate complexes **1** and **2**

Complex	Burn temperature, K
$[Cu((CH_2)_5CN_4)_4](ClO_4)_2$	1451
$[Co(NH_3)_5(C_6H_{10}N_4)](ClO_4)_3$	2329

Table 4. The calculated composition of principal burning products of perchlorate complex **1**

Burning product	Concentration, mol kg^{-1}
C(condensed)	18.270
Cu(condensed)	1.218
HCl	2.444
N_2	9.788
H_2	17.459
CH_4	2.436
CO	8.534

Trace amounts of the following burning products: CO_2 -0.184 mol kg^{-1}, H_2O-0.910 mol kg^{-1}, HCN-0.013 mol kg^{-1}, NH_3 -0.040 mol kg^{-1} are shown to be present.

Table 5. The calculated composition of principal burning products of perchlorate complex **2**

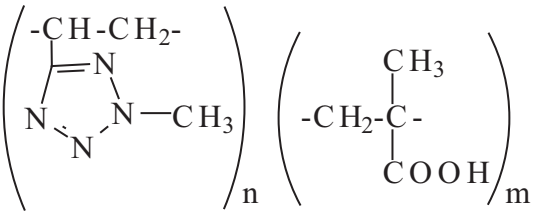
Burning product	Concentration, mol kg^{-1}
Co(condensed)	1.468
HCl	4.684
N_2	7.749
H_2O	8.957
H_2	10.206
CO	8.964
CO_2	1.369

Trace amounts of the following burning products: NH_3 0.003 mol kg^{-1}, $CoCl_2$ 0.235 mol kg^{-1} are shown to be present.

The above regularities in the calculated composition of main burning products of perchlorate complexes **1** and **2** may be the result of strongly negative oxygen balance of the salts (the oxygen balance of perchlorate complex **1** equals to -117.77%, the oxygen balance of perchlorate complex **2** equals to - 33.07%).

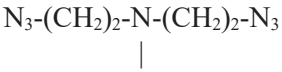
Perchlorate complexes as the modifiers of burning processes in solid rocket propellants

One of the promising ways of regulating ballistic characteristics of highly filled energetic formulations is the addition of burn modifiers. Complex compounds of d-metals are effective modifiers of the burning [4]. An energetic copolymer of 2-methyl-5-vinyltetrazole with methacrylic acid (PVMT) (Technical Specification –38-403-208-88) was used as a high-molecular binder for a model solid rocket propellant formulation.



PVMT

A liquid aliphatic azide, 1,5-diazido-3-nitro-3-azapentane (**3**) was used as active plastisizer of the polymer base (Technical Specification – 13-01-76) [4, 5].



1,5-Diazido-3-nitro-3-azapentane

Plastisizer **3** has the density of to 1.344 g cm^{-3}, and value of the enthalpy of formation ΔH_f^0 = 3025 kJ kg^{-1}.

Model formulations had the following composition: ammonium perchlorate of bimodal granulometric composition: grade «C» (< 50 μm) – 32%; grade «A» according to Technical Specification – 84-942-82 ($S_{specific}$ = 12000 $cm^2 g^{-1}$) – 32%, fuel - aluminum powder of grade ACD – 6 ($S_{specific}$ = 6000 $cm^2 g^{-1}$) – 6%, binder and plastisizer – 28%, additions of the complexes were introduced into the formulations in amount of 2%. Ballistic tests were made in a constant pressure bomb. Results of ballistic tests are presented in Table 6.

Table 6. Effect of additions of perchlorate complexes **1** and **2** on the burning of a model propellant

Index of formulation	Equation of deflagration $U=A\cdot P^{\upsilon}$		U_{10}, mm s^{-1}	U_4, mm s^{-1}
	A	***υ***		
Basic formulation	11.1	0.71	47.2	26.6
$[Cu((CH_2)_5CN_4)_{4)})](ClO_4)_2$	16.1	0.56	58.4	35.0
$[Co(NH_3)_5((CH_2)_5CN_4)](ClO_4)_3$	10.5	0.60	41.8	24.1

U_{10}- rate of burning at 10 MPa pressure;
U_4- rate of burning at 4 MPa pressure.

The results obtained permit to make the following conclusions:

- The pressure exponent of burn rate law in the presence of additions decreases from 0.71 to 0.60-0.56 and this is an indirect confirmation of the fact that these additions affect the burning processes in the condensed phase.
- Complex perchlorate **1** increases the burn rate of a model propellant by 35.5%.

Therefore. the prepared energetic complexes are promising modifiers of the burn rate and can be used in the development of solid rocket propellant formulations.

Acknowledgments

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