Design and Combustion Behaviour of Explosive Coordination Compounds

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ABSTRACT

Explosive coordination compounds are a subject of considerable interest because some of them have found specific applications, in particular, as safe primary explosives or igniters. The present work focuses on general principles of designing explosive coordination compounds. Effect of the complex molecule's constituents on explosive and physicochemical properties is considered. The main classes of organic compounds which might be used as ligands of explosive complexes are discussed. Since the burning rate of an explosive compound is thought to be an important characteristic determining such properties as deflagration-to-detonation transition and initiating efficiency, the work deals with studying the relationship between chemical structure and burning rate characteristics of explosive complexes. The burning rate of optimally designed coordination compound depends mainly on two factors: nature of oxidizers and nature of the central metal atom. Changeover from nitrate ion to perchlorate one usually raises the burning rate by a factor of 10 and more. Metal atom included in complexes can serve not only as a matrix, which ties up ligand-fuel and anion-oxidizer, but also as a catalyst of redox reactions occurring during combustion. It is found that each anion-oxidizer has its own set of metals that possess a catalytic activity. In the light of the experimental findings, a plausible combustion mechanism of coordination compounds has been suggested.

NOMENCLATURE

Q_v	Heat of explosion at constant volume, kcal/kg
T_f	Adiabatic flame temperature, K
U_m	Mass burning rate, $g/cm^2.s$
P	Pressure, MPa
E_o	Standard redox potential, V
CC	Coordination compounds
CN	Coordination number
M	Metal atom
L	Ligand
(L - H)	Ligand intermediate after removing H atom
(L - 2H)	Ligand intermediate after removing two H atoms
OX	Anion of oxygen-containing acid
X	Anion after removing O atom from OX anion
At	4-amino-1,2,4-triazole
En	Ethylenediamine

1. INTRODUCTION

Chemical structure of coordination compounds (CC) of the common formula of $[ML_n](OX)_m$, where M is central metal atom, L is ammonia or organic base (ligand), and OX is anion, makes it possible to create substances capable of explosion. Although these coordination compounds are known for more than 70 years[1,2] and also some of them have found specific applications, in particular, as safe primary explosives or igniters,[3,4] the principles of designing explosive CC are not practically discussed in literature. In a few works[5,6] dealing with a relationship between CC structure and explosive properties, it has been found that CC represent an extremely wide range of explosives. Explosive CC as well as many other energetic materials are known to be capable of self-sustained burning. CC of this sort may be considered as energetic compositions, in which metal atom, fuel and oxidizer are mixed at molecular level. The possibility of significant variations in the nature of CC along with the presence of metal atom, which can act as a burning catalyst suggests a wide range of the conceivable burning rates of CC. The combustion

parameters, in turn, have been shown for high and primary explosives to be responsible for such explosive property as deflagration-to-detonation length[7]. For priming compositions, this is the main index of initiating efficiency.

This has provided the two goals of our work: learning various ways of the explosive coordination compound design and clarifying how their chemical structure can affect the burning rate.

2. EXPERIMENTAL DETAILS

All complexes investigated in this work were of reagent grade. Parameters of the steady-state combustion of all energetic materials were measured in a window constant-pressure vessel in the pressure range of 0.1-40 MPa using a photographic recording. The substances under investigation were compacted into transparent acrylic tubes at 250 MPa to give pressed strands.

A unique procedure of preparing high-density strands was devised for measuring the burning rates of fast-burning explosives[8]. A substance was compacted in the form of pellets 10 mm in diameter and 1-1.5 mm thick under a pressure of 500-600 MPa. Plates of about 2 mm width were cut from the pellets. Before burning, the plate was positioned vertically in a beaker filled with a liquid epoxy resin which prevented flame propagation along the side surface.

3. DESIGN APPROACH OF THE EXPLOSIVE COORDINATION COMPOUNDS

To be capable of explosion and combustion the coordination compounds should contain such molecular fragments that, either themselves or their destruction products, possess oxidizing properties. These fragments usually are ClO_4^-, NO_3^- and similar counter ions. Metal atom serves as a matrix, bonding together a fuel-ligand and an oxidizer. Nature of metal atom controls stability of CC and amount of combustible and oxidizing fragments per metal atom. A basis for designing such a type of CC is making a choice of ligand which provides not only the fuel-oxidizer ratio and, consequently, heat of explosion, but also CC chemical stability.

3.1 Central Metal Atom

For selection as an explosive, a compound should have unvarying composition and be stable under ambient conditions in the solid state. This requirement for CC is mainly ensured by the nature of central metal atom[9]

Thus, alkali metals have little tendency to complex formation. Compounds with oxygen-containing ligands are typical for having such a property. Compounds with nitrogen-containing ligands, which are most interesting from the point of view of making explosive CC, are usually very sensitive to moisture. The perchlorate complexes with hydrazine are known only for Li and Na having a strong tendency of complex formation among alkali metals[10].

In comparison with alkali metals, alkaline-earth ones possess a noticeably larger tendency to complex formation. Be^{2+} as well as Al^{3+} of the next group, however, need to be excluded from the consideration because of their tendency to form stable hydroxo- and oxo-complexes of non-explosive nature due to the small sizes of the metal ions. Other alkaline-earth metals also show a strong tendency to bind with oxygen; therefore, the complexes even with chelating ligands are usually hygroscopic and often contain water in their composition.

Cr, Mn, Fe, Ni and Co transition metals are "working horse" of coordination chemistry. Salts of the bivalent metals form stable complexes with various organic compounds. CC of Cr(III) and Co(III) are also well known for their stability. Other transition metals in this valency state show strong oxidizing properties which cannot be reduced by coordination to suitable neutral ligand. Therefore, it is impossible to obtain CC owing to redox reactions between the metals and ligands. Iron(III) also is capable of forming complexes with neutral nitrogen donors but many of them are decomposed by water at standard conditions. Iron(II) complexes are thermodynamically unstable with respect to atmospheric oxidation.

Metals of Group I and Group II such as $Cu, Ag, Zn,$ and Cd can form stable compounds. However, because of high cost, the use of Ag as well as of transition metals of other rows in Periodic Table is not preferred in synthesis of explosive CC; therefore, they are not considered here. Among heavy metals, Pb attracts attention because of its well-known catalytic properties. Pb salts with nitrophenols possess initiating ability[11].

The valence of central metal atom defines a sum of oxidizing groups, whereas the coordination number (CN) of metal controls the fuel contents in the molecule. Changes in the valence of metal atom and its CN both allow to regulate the fuel-oxidizer ratio. As seen from

Li 4	Be	B											
Na 4	Mg 6	Al	Si										
K	Ca 6	Ga	Ge	Sc	Ti	V	Cr^{II} 6 Cr^{III} 6	Mn^{*} 6	Fe^{II} 6 Fe^{III} 6	Co^{II}4,6 Co^{III} 6	Ni^{II}4,6	Cu^{II}4,6	Zn 4,6
Rb	Sr 6	In	Sn	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd 4,6
Cs	Ba 6	Tl	Pb^{II}4,6	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Figure 1. Location of the metals in the Periodic Table, that might be used in synthesis of explosive coordination compounds (marked with bold *font*). The Roman numbers indicate the valencies, Indo-Arabic figures indicate common coordination numbers.
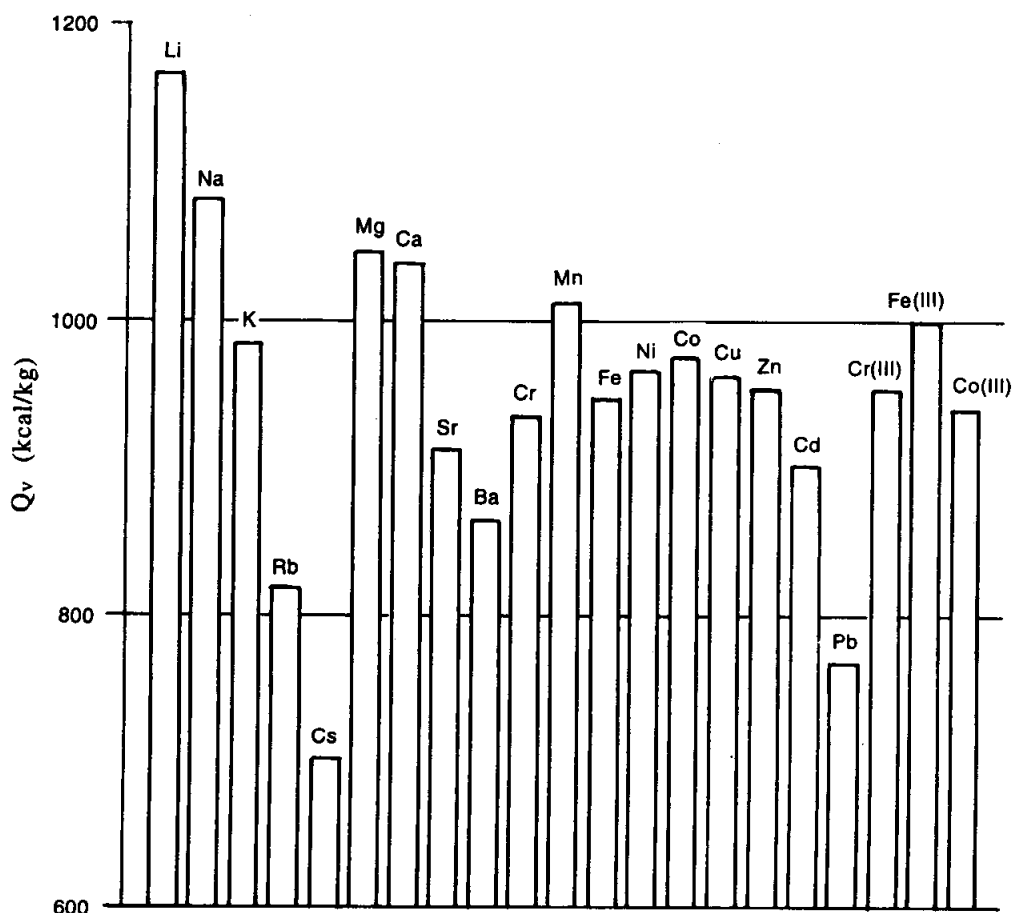
Figure 2. Heats of explosion of complexes of metal perchlorates with a tentative ligand CH_4N_6.

Fig.1, most of the chosen metals are bivalent, and only Cr, Co and Fe show bivalent and trivalent state. A number of metals, such as Cu, Ni, Zn and Cd permit syntheses of CC with various numbers of ligands in the molecule. For example, 4-amino-1,2,4-triazole is able to coordinate to both copper perchlorate and nitrate to form CC with two (CN = 4) or three (CN = 6) ligands, CuL_2X_2

and $CuL_3X_{212,13}$. The fuel-oxidizer ratio exerts a major effect on energetic characteristics of explosive CC. Besides, CC energetic characteristics may vary with the change of metal atom due to different enthalpies of cation formation and heat of coordination. Heats of explosion calculated for coordination compounds of various metal perchlorates with a tentative ligand of

373

CH_4N_6 formula like 1,5-diamino tetrazole. The enthalpy of formation of which is accepted to be O kcal/mol, are shown in Fig. 2. In order to balance the fuel-oxidizer ratio the calculations have been performed under the assumption that compounds of monovalent metals contain one ligand, CC of divalent and trivalent metals contain two and three ligands, respectively. From the heat of explosion standpoint, the metal in CC is a ballast; the heat of explosion falls as the metal atom mass increases. For example, passing from Li to Cs, the heat of explosion decreases from 1155 to 704 kcal/kg. The effect of different enthalpies of formation of metal cations will be seen in a comparative analysis of CC with metals of close mass Na-Mg, K-Ca, Rb-Sr and Cs-Ba. The effect of chemical peculiarities of metals may be well illustrated by Cr and Co transition metals. A characteristic of combustion and explosion processes of $Cr(II)$ and $Cr(III)$ complexes is formation of oxides of Cr and lower heats of explosion than for $Mn(II)$ and

$Fe(III)$ complexes yielding halides under these conditions.

This composition corresponds to 1,5-diaminotetrazole, as an example. $Co(III)$ complex, unlike $Fe(III)$ one, yields chloride of divalent metal which is far less preferred from the energy release standpoint.

It is known that CC can be divided as inert (based on trivalent metals) and labile (based on bivalent metals) compounds with respect to elimination of the ligands[9] From the point of view of designing explosive CC, metals in 3+ oxidation state have ability to form more stable CC, as well as the capability to form CC with dissimilar ligand environment, that allows regulation of not only physicochemical properties of CC but also that of fuel-oxidizer ratio. Well-known (5-cyanotetrazolato) penta-amine cobalt(III) perchlorate (CP) and related compounds may serve as examples[3,4,14] Thus, CP
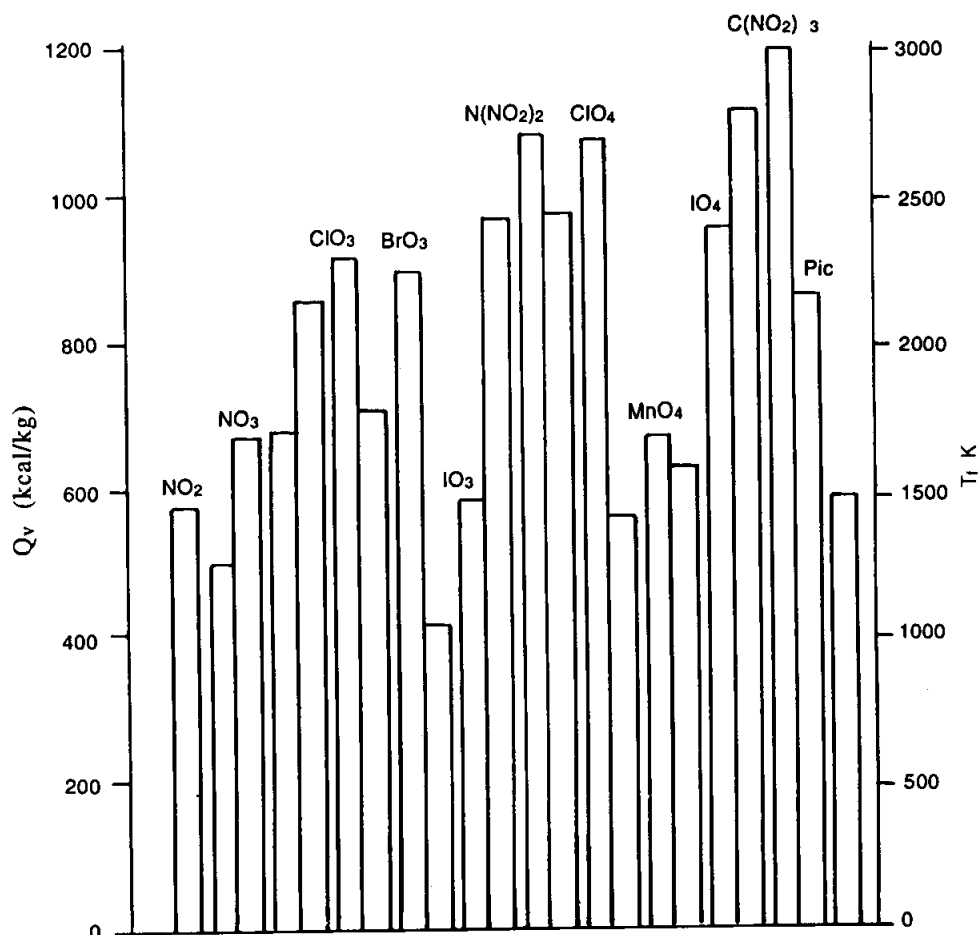

Figure 3. Heats of explosion and adiabatic flame temperatures at 10 MPa for complexes CoL_2X_2 with a tentative ligand CH_4N_6. Light and dark bars relate to Q_v and T_f, respectively.

contains ammonium ion and anion of cyanotetrazole as ligands.

3.2 Anion

Anions in the complexes under consideration play the role of oxidizer. These may be anions of familiar oxidizing acids, such as ClO_4^-, ClO_3^-, NO_3^-, NO_2^-, IO_3^-, IO_4^-, BrO_3^-, MnO_4^-, as well as various nitro-containing compounds, such as $C(NO_2)_3^-$, $N(NO_2)_2^-$ and picrate (Pic⁻). They differ in the content of active oxygen and enthalpy of formation that significantly influence the energetic performance of CC (Fig. 3). Very frequently the chemical nature of an anion affects the number of ligands in CC. The reason is that such anions as NO_2^-, NO_3^-, and very seldom ClO_4^- enter into the inner coordination sphere of the metal thus decreasing sites accessible for ligands. What is more important, the nature of anion has a major effect on such physicochemical and explosive properties of CC as solubility, thermal stability, flash point, impact sensitivity[6]. Such anions as NO_2^-, IO_3^-, IO_4^-, BrO_3^-, MnO_4^- exhibit extreme oxidizing properties even at room temperatures resulting in a significant limitation of the number of ligands which may be introduced in the reaction of complex formation. Even with such hard oxidizable ligand as NH_3, complexes formed with the above mentioned anions prove to be of low thermal stability and dangerous in handling.

Therefore, despite the fact that a choice of an anion affects considerably the heat of explosion, first it is necessary to learn how the physicochemical properties of CC with a chosen anion will comply with the final task. For instance, complexes with high-reactive anions of type ClO_3^-, IO_4^-, BrO_3^-, MnO_4^- may possess initiating ability, however, the other properties, such as thermal stability or solubility, may turn out to be unsuitable. Complexes with anions of nitrocompounds are usually insoluble in water and possess high heat of explosion; however, it is difficult to find out substances with initiating efficiency among them because of low reactivity of the anions.

3.3 Ligand

Since the content of an oxidizer in the molecule of explosive CC is limited (in most cases it is 6-8 oxygen atoms), a ligand consisting of minimal numbers of C and H atoms is required for high-energy materials to be obtained. Besides, it must contain a donor atom, usually N, O or S. Depending on the position in the Periodic

Table, metals possess varying tendency to bind these atoms. However, since only neutral complexes are treated here, the basicity of the donor atoms becomes the most important factor and here nitrogen atom is beyond the competition (for example, pK_a of RNH_2 ~8-11, R_2S ~5, R_2O ~ 0-3). If ordinary non-exotic compounds stable in common conditions is considered, it is obvious that S and O atoms can take part in complex formation only together with N atom as polydentate ligand constituents. Polydentate ligands and, especially chelating ligands are of most interest, since a great increase in stability of CC is observed[9].

Ligand design can be viewed as the selection between desired low content of C and H atoms, high enthalpy of formation and high reactivity of the ligand, on one hand, and necessary strong basicity of its donor groups, possibility of chelating and resistance to oxidation at room temperature, on the other hand.

It remains to be seen what classes of organic bases are the most attractive for tailoring explosive CC. Ammonia and its organic derivatives are the most well-known simple ligands (I, Fig. 4). However, gaseous ligands like ammonia and light organic amines form stable-in-standing CC only with inert-to-substitution metals like $Cr(III)$ and $Co(III)$. Increasing the aliphatic moiety is not helpful since it decreases the energy of CC.

Polydentate amines (II, Fig. 4), simplest representative of which is ethylenediamine (En), form stable CC with many metals. However, as in the previous case, the possibility of varying ligand composition is very limited.

Compounds, in which nitrogen donor atom is tied by double bond with carbon (sp^2-hybridization) have the
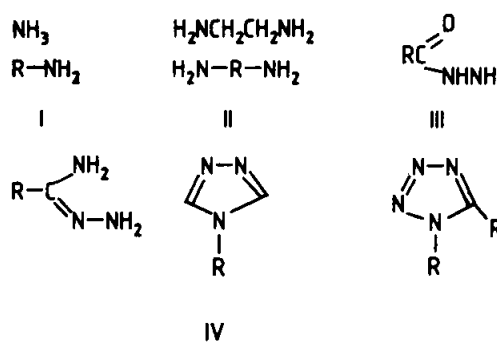

Figure 4. Main classes of organic substances that might be used as ligands for synthesis of explosive coordination compounds.
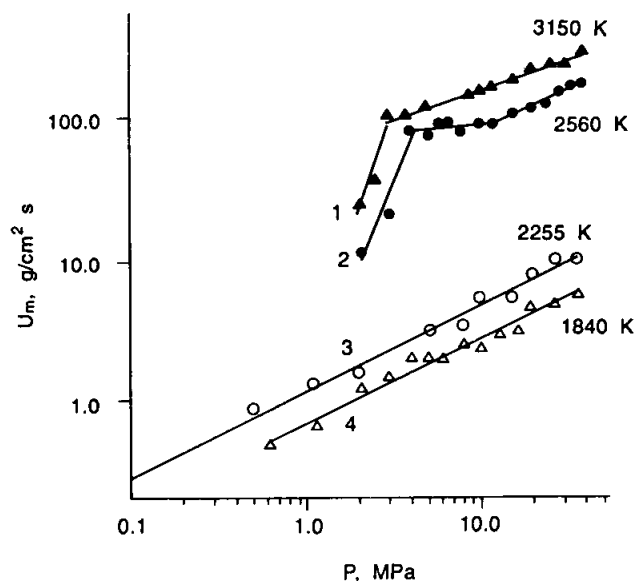
Figure 5. Effect of adiabatic flame temperature on the burning rate of coordination compounds of 4-amino-1, 2, 4-triazole with copper perchlorate and nitrate: 1 - [CuL2](ClO4)2, 2 - [CuL3](ClO4)2, 3-[CuL2](NO3)2, 4- [CuL3](NO3)2.
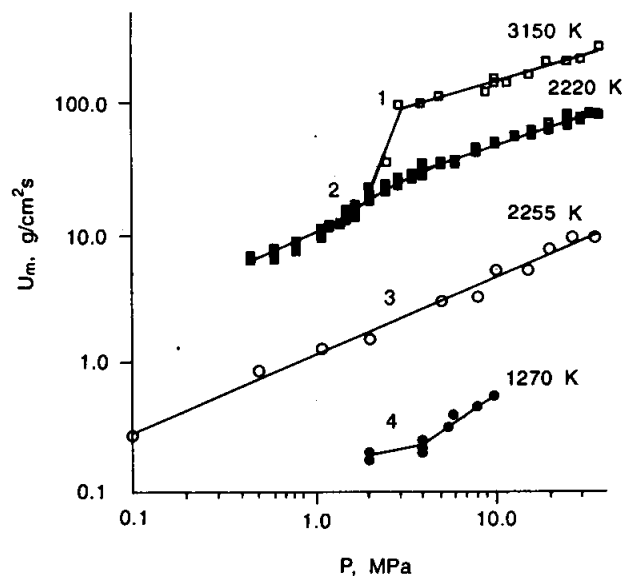

Figure 6. Burning rate vs. pressure for coordination compounds of 4-amino-1,2,4-triazole (At) and ethylenediamine (En) with copper perchlorate and nitrate: 1-[CuAt2](ClO4)2, 2-[CuEn2] (ClO4)2, 3-[CuAt2](NO3)2, 4-[CuEn2](NO3)2.

possibility of additional π-donating interaction with transition metals having unfilled d-orbitals. This allows stable CC based on relatively weak donors like various polynitrogen heterocycles and amidrazones[13,15] (IV, Fig. 4) to be synthesized. These compounds are very useful for obtaining high energy CC, since many of them possess high enthalpy of formation.

The hydrazides of carboxylic acids (III, Fig. 4) are likely to represent one of the most interesting class of ligands, which are capable of not only forming CC with a wide range of metals due to the presence of two donor atoms (O and N) and formation of stable five-membered metalcycle, but also offering a strong possibility to manipulate the composition[16-19]

From this analysis it is clear that design of high energy stable CC consists of searching for a compromise between such contradictory requirements as high reactivity of oxidizer and thermal stability of CC; high enthalpy of formation of ligand and its basicity; heat of explosion of CC with a given metal and the chemical stability of CC under normal conditions.

4. COMBUSTION BEHAVIOUR OF EXPLOSIVE COORDINATION COMPOUNDS

Main factors which can affect the burning rate of explosive CC are adiabatic flame temperature and nature

of CC components viz. metal, anion and ligand. Since redox transformations form the basis of combustion, the burning rate may be considered to depend both on reactivity of fuel-ligand and oxidizer-anion. Metal atom introduced in this redox system at the molecular level may play a role of combustion catalyst.

4.1 Ligand

As mentioned above, the composition of ligand influences the fuel-oxidizer ratio, which, in turn, controls the combustion temperature. Adiabatic flame temperature may be correlated with the burning rate studies for complexes of copper perchlorate and nitrate with 4-amino-1,2,4-triazole (Fig. 5). In this case, complexes may be considered to contain the same metal, anion and ligand and differ only in the fuel-oxidizer ratio, and consequently in the combustion temperature.

It can be readily seen from Fig. 5 that the higher the combustion temperature the more the burning rate. An enhancement of CC burning rates in the changeover from ethylenediamine to 4- amino-1,2,4-triazole (Fig. 6) may probably be explained only by alteration in the CC adiabatic flame temperature. No significant effect of the ligand reactivity on burning rate has been found. It is believed to be connected with the presumption that the ligands take no part in the rate-limiting stage. Another
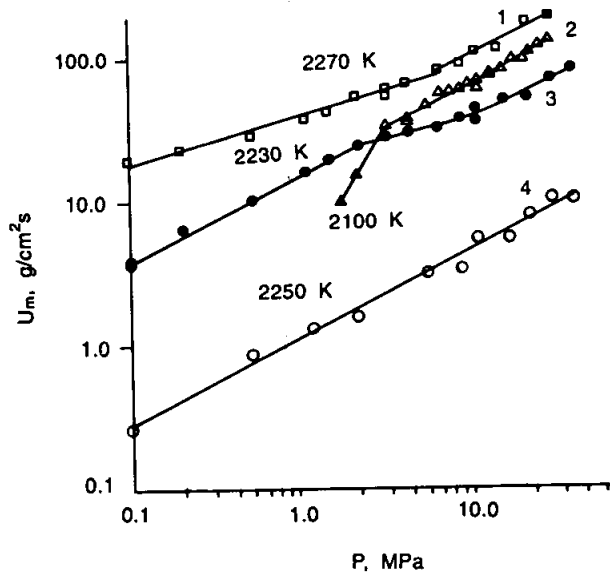
Figure 7. Effect of the anion nature on the burning rate of coordination compounds of 4-amino-1,2,4-triazole with copper bromate $[CuL_3](BrO_3)_2$ (1), perchlorate $[CuL_4(H_2O)](ClO_4)_2$ (2), chlorate $[CuL_3](ClO_3)_2$ (3), and nitrate $[CuL_2](NO_3)_2$ (4).
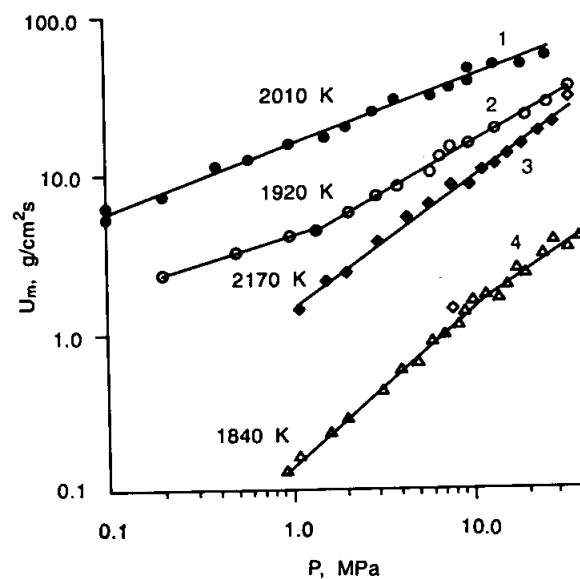
Figure 8. Effect of the anion nature on the burning rate of coordination compounds of 4-amino-1,2,4-triazole with zinc bromate $[ZnL_3](BrO_3)_2$ (1) and chlorate $[ZnL_3](ClO_3)_2$ (2), hydrazide of 5-amino-2- tetrazolylcarboxylic acid with zinc perchlorate $[ZnL_2](ClO_4)_2$ (3), semicarbazide with zinc nitrate $[ZnL_2](NO_3)_2$ (4).

alternative explanation is that the rate-determining stage involves ligand destruction product of close reactivity rather than the ligands themselves.

4.2 Anion

As seen from Fig. 5 and Fig. 6, by the changeover from nitrate anion to perchlorate one raises the burning rate to a greater extent than adiabatic flame temperature. Fig.3 shows that the nature of anion influences both the heat of explosion and the adiabatic flame temperature to a large extent. However, as early as the 70's A.E. Fogelzang showed that the burning rate of ammonium salts of various inorganic oxidizing acids was determined mainly by the oxidizer reactivity rather than the adiabatic flame temperature or thermal stability of compounds[20]. The effect of oxidant activity is clearly observed for combustion of ammonium complexes of copper too[21]; however, since anion reactivity and flame temperature affect the burning rate in the same manner, the authors have come to the conclusion that the burning rate of CC is chiefly determined by the adiabatic flame temperature alone. Complexes of 4-amino-1,2,4-triazole obtained recently allow choosing and comparing burning rates of compounds having close combustion temperatures[12,13]. As readily seen from Fig. 7 & 8, burning rates of CC depend very much on the nature of anion. As in the case of salts with oxidizing acids, the

anion reactivity may be estimated in terms of standard redox potential[20]. The complexes of BrO_3^-, ClO_3^- and ClO_4^- anion-oxidizers having the greatest redox potentials and, respectively, the greatest reactivity, exhibit the highest burning rate values. As shown in previous works[22,23], there exists a direct correlation between redox potential of reagents in the combustion wave and free activation energy of rate-limiting redox reactions. The results of the present work suggest this correlation to be true for combustion of CC.

It is noteworthy that an order of increasing explosive sensitivities of ammonium complexes $[Co(NH_3)_6](OX)_3$ obtained from Joyner's data[6]: $OX = NO_3^- < IO_3^- < NO_2^- < ClO_4^- < ClO_3^- < BrO_3^- < MnO_4^-$ is consistent with the order of increasing redox potential of corresponding acids24. It is believed that the oxidizer activity plays as important a role in the impact sensitivity as it affects the burning rate.

4.3 Central Metal Atom

It is important to note that the effect of the metal atom on the adiabatic flame temperature differs significantly from the effect on the heat of explosion. In the latter case, metal ion plays a role of ballast; and increase in the metal atom mass results in decrease in the
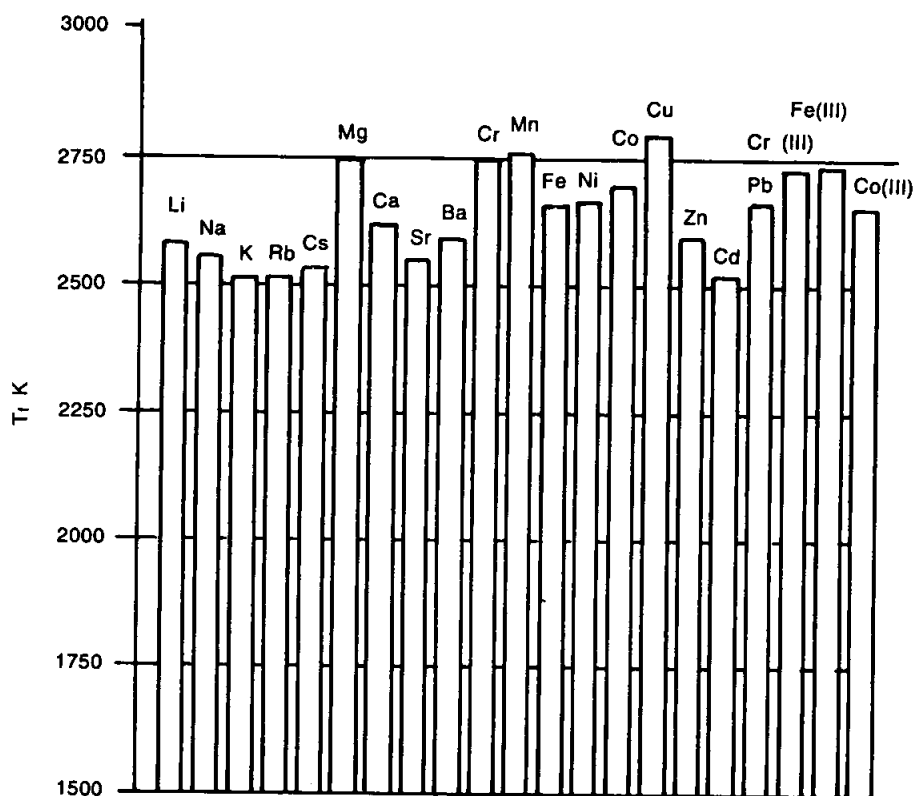
Figure 9. Adiabatic flame temperatures of coordination compounds of metal perchlorates with a tentative ligand CH_4N_6.

heat of explosion. The combustion temperature does not undergo significant variations, because a decrease in the heat of combustion with increasing metal atom mass is compensated by an increase in the metal heat capacity. For instance, while a set of metals exhibits variation in the heat of explosion as much as 50 per cent (Fig. 2), the variation in the flame temperature does not exceed 10 per cent (Fig. 9).

Unlike the adiabatic flame temperature, the nature of metal affects the burning rate to a large extent. Each anion-oxidizer has been shown to possess its own set of metals, coordination compounds of which burn faster than salt of ligand and corresponding oxidizing acid[25]. This research work clearly indicates that some metals were catalysts of combustion while others were not. Thus, during combustion of perchlorate complexes Ni, Co, Cu, Cd and Pb display catalytic properties, whereas combustion of nitrate ones is catalyzed only by Cu and Pb. Fig.10 can serve as a good illustration of the effect of metal nature on burning rate, in which burning rate data of all studied CC of copper perchlorate, $[CuL_n](ClO_4)$, along with data on combustion of both organic perchlorates $L.nHClO_4$ (where L = hydrazides of carboxylic acids and aliphatic amines) and CC of alkali

metal (Li and Na) and alkaline-earth metal perchlorates (Mg, Ca, Sr and Ba) is plotted. It is seen that at every combustion temperature, complexes of copper burn
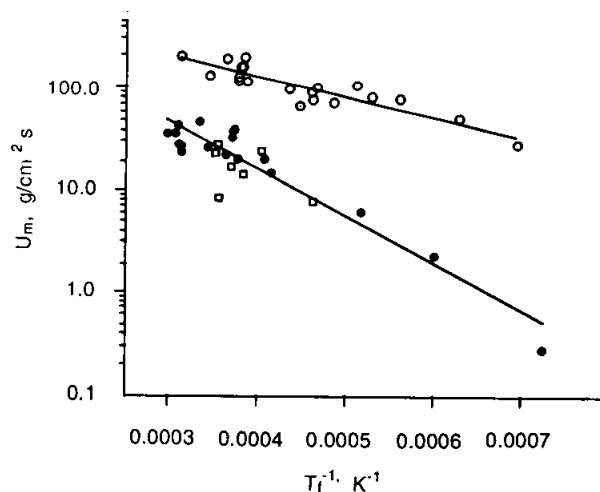

Figure 10. Effect of adiabatic flame temperature on the burning rate at pressure 20 MPa: o - coordination compounds of copper perchlorate $[CuL_n](ClO_4)$ ● - perchlorates of aliphatic amines and of hydrazides of carboxylic acids, □ - coordination compounds of alkali and alkaline-earth metal perchlorates.

faster than related non-metal systems, while combustion data of CC of alkali and alkaline-earth metals depend on the temperature dependence of burning rate of organic perchlorates. Ni, Co, Cd and Pb perchlorate complexes also burn faster than related non-metal system at all temperatures. Coordination compounds of lead and copper nitrates give a similar pattern when compared with parent organic nitrates. Combustion data for CC of metal bromates, chlorates and iodates, few as they are, indicate a like set of metal catalysts as for CC of metal perchlorates.

5. COMBUSTION MECHANISM OF EXPLOSIVE COORDINATION COMPOUNDS

A dramatic effect of oxidizer on the burning rate of CC is believed to indicate conclusively that the slowest stage of combustion involves redox reactions, whereas the rate of the initial decomposition reaction is subject to the rate of the subsequent oxidation stage. The presence of metal atoms in these systems results in the fact that certain compounds burn faster than the control. The enhancement of the burning rate is attributable to the catalytic action of some metals during the redox process.

Let us consider possible chemical processes occurring during combustion of CC. Obviously, there are various paths depending on whether or not the metal atom takes part in redox conversions (Fig.11). Such metal ions like Li^+, Na^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, etc., practically cannot be oxidized by chemical oxidizers.

Consequently, in this case the central metal atom serves only as a matrix. Insofar as anions possess relatively weak oxidizing properties, it may be suggested that ligand is oxidized by anion destruction products which are more reactive than anions. A support for such suggestion derives from the fact that alkali and alkaline-earth metal complexes and organic salts of oxidizing acids have close burning rates at the same temperature (Fig.10). There would not be this closeness of burning rates if kinetics of rate-limiting stage were determined by the reactivity of acid and anion.

It is known that such oxidizing acids as $HClO_4$ or HNO_3 decompose at high temperature onto ClO_3^*, NO_2^* and OH^*. As shown in previous works,[26-28] a destruction of NO_3^- and BrO_3^- anions results in homolysis of the Hal-O and N-O bonds to form oxygen radical anion O^{-*}:

$$NO_3^- \rightarrow O^{-*} + NO_2^*$$
$$BrO_3^- \rightarrow O^{-*} + BrO_2^*$$

or in general:

$$OX^- \rightarrow O^{-*} + X^* \tag{1}$$
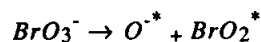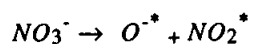
Destruction products of acids and anions differ insignificantly in the reactivity resulting in a closeness of burning rates. Thus, the initial stage of ligand oxidation in CC with non-oxidizable metals can be schematically represented by:
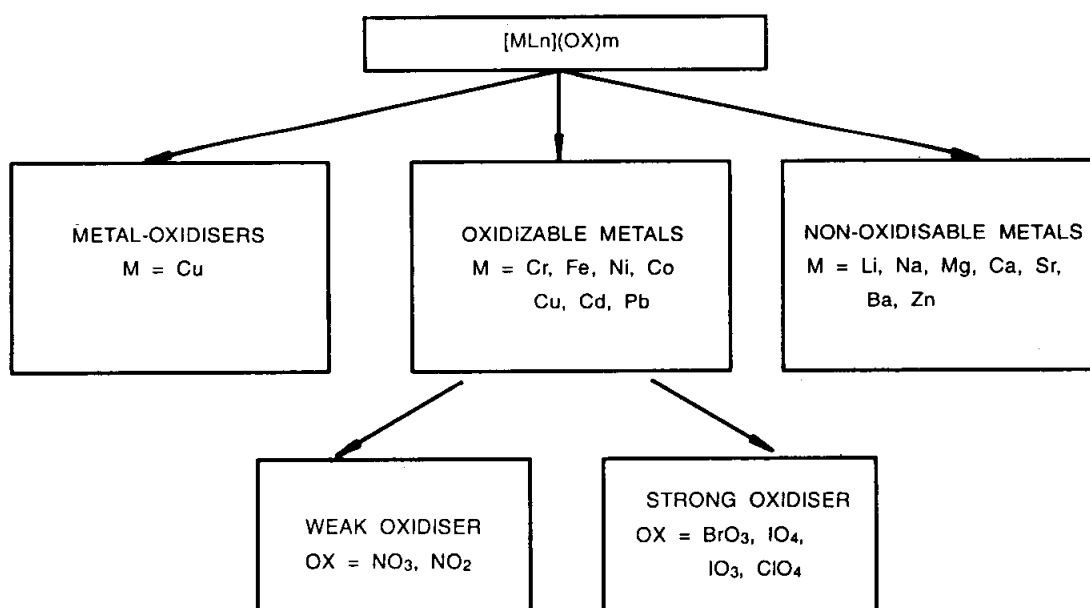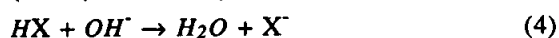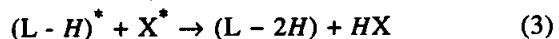

Figure 11. Groups of coordination compounds with different combustion mechanisms.

Scheme I

$$L + O^{-*} \rightarrow (L - H)^* + OH^- \qquad (2)$$

$$(L - H)^* + X^* \rightarrow (L - 2H) + HX \qquad (3)$$

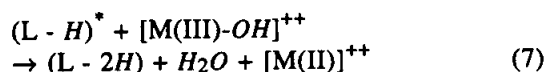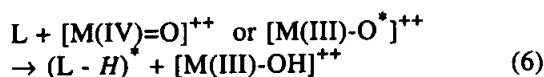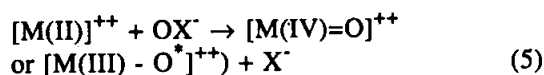$$HX + OH^- \rightarrow H_2O + X^- \qquad (4)$$

This cycle may further be repeated with X^- and (L - 2H) species. The main result of the above cycle is essentially dehydrogenation of the ligand and removal of an oxygen atom from the anion with the formation of water. Since the oxygen atom acts formally as an oxidizer, the oxidation process involves a two- electron transfer. The two- electron oxidation of the ligand by the one-electron oxidant O^{-*} requires a removal of the second electron by X^* radical followed by fast neutralization process. It means, in this instance, the rate of heat release in the oxygen reduction process is defined by rate constants of the reactions (2), (3) and (4). The values of rate constants of the reactions (2) and (4) remain unchanged for all the anions, whereas value of the rate constant of the reaction (3) depends on the reactivity of X^* radical. This is in good agreement with the observed alteration in the burning rate while passing from one anion to another.

If the metal atom can change its valence state, the interaction between M(II) and anion in the combustion wave is considered to yield an oxygen-containing species including the metal of a high-valence state, which may be depicted either as a complex of M(III) with coordinated anion radical, $[M(III)\text{-}O^*]^{2+}$, or as an oxocompound of metal(IV), $[M(IV)=O]^{2+}$. The species as the main active site has been described in the studies dealing with modeling ferment reactions of oxidation[29-31]

Hence, the general mechanism consistent with the observed combustion behaviour of CC is oxygen rebound from anion to the ligand via a metal-oxo intermediate:

Scheme 2

$$[M(II)]^{++} + OX^- \rightarrow [M(IV)=O]^{++}$$
$$\text{or } [M(III) - O^*]^{++}) + X^- \qquad (5)$$

$$L + [M(IV)=O]^{++} \text{ or } [M(III)\text{-}O^*]^{++}$$
$$\rightarrow (L - H)^* + [M(III)\text{-}OH]^{++} \qquad (6)$$

$$(L - H)^* + [M(III)\text{-}OH]^{++}$$
$$\rightarrow (L - 2H) + H_2O + [M(II)]^{++} \qquad (7)$$

The catalytic conversion cycle differs from non-catalytic one (Scheme 1) in that the ligand is oxidized by highly active metal-containing species in accordance with reactions (6) and (7). These species have been shown by numerous studies on catalysis of oxidation reactions to be more active towards a reductant than the original oxidizer itself[29-33]

According to the mechanism proposed, only metals capable of forming high-valent metal oxo-species can produce the catalytic effect. The stronger the oxidative properties of anion, the larger the body of metals capable of the catalytic activity. For example, among perchlorate complexes even $Cd(II)$ (E_o $Cd2+/3+$ ~ 3 V) exhibits the catalytic activity, whereas for nitrate complexes only lead (E_o $Pb^{2+/4+}$ ~ 1.7 V) can catalyse combustion. It should be noted that oxidation of the metal to such uncommon valence state is possible only with the coordination surrounding that can stabilise a high-valence state of the metal[34].

In the case of weak oxidizers such as a nitrate anion (E_o NO_3^-/NO_2^- = 0.01V) unlike strong halate oxidizer (E_o ~ 0.6V) rate of reaction (5) is small, so that the rate-limiting stage is oxidation of ligand by anion (Scheme 1). This is confirmed by the fact that presence of oxidizable metal ions cannot result in increase in the burning rate. The exception is CC of lead and copper. Lead is characterised by the lowest redox potential for M(IV) valence state. Oxidation of $Pb(II)$ in its ligand environment to $Pb(IV)$ is possible to proceed rapidly even with weak oxidizers. Another possible explanation of increased burning rates of lead nitrate complexes is catalysis of oxidation reactions of nitrogen oxides by lead ions, as in the combustion of catalysed double base propellants[35-37].

The catalytic effect like that observed for combustion of complex compounds of copper nitrate is characteristic of metals having oxidizing properties (E_o $Cu^{3+/2+}$ = 0.15 V). In the combustion wave, $Cu(II)$ is able to oxidize ligand-fuel L to form the cation-radical L^{+*} which, in turn, splits out a proton to form $(L\text{-}H)^*$ radical according to :

$$Cu(II) + L \rightarrow Cu(I) + L^{+*}$$

$$L^{+*} + NO_3^- \rightarrow (L\text{-}H)^* + HNO_3$$
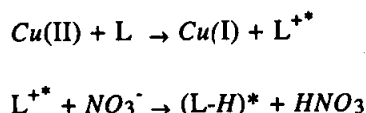
This results in appearance of strong oxidizer HNO_3 instead of weaker oxidizer NO_3^-, on reaction with $Cu(II)$

followed by fast ligand oxidation by the highly active metal-containing species in accordance with reactions (6) and (7) occurring faster than ligand oxidation by destruction products of anion or HNO_3.

5. CONCLUDING RFMARKS

The task of synthesis of high-energy explosive CC can be divided into three parts: (i) anion selection, which defines main physicochemical and explosive properties of CC, such as solubility, explosion temperature, explosive sensitivity, burning rate; (ii) metal ion selection, which determines largely the chemical stability of CC and the burning rate; and (iii) ligand selection, which defines chemical stability of CC and, mainly, heat of explosion.

Search for a compromise between the desired explosive properties and necessary requirements on physicochemical characteristics is the basis for designing explosive CC.

The burning rate of explosive CC is determined by kinetics of redox reactions and is altered in a very wide range due to significant variations in the oxidizer reactivity as well as involvement of metal atom in redox reactions. Since the combustion parameters are important for priming composition and igniters, a knowledge of the relationship between the burning rate level and structure of explosive CC permits a reasonable search and syntheses of these compounds.

REFERENCES

1. Friederich & Vervoorst, Z.ges. Schiess.-Sprengstoffw., 1926,21, 49-143.

2. Cook, M.A.; Davis, C.O. & Lawson, W.E. Ammonium nitrate explosives. British patent 544,582. 1942.

3. Lieberman, M.L. & Fronabarger, J.W. Status of the development of 2-(5-cyanotetra-zolato) pentaamine

cobalt(III) perchlorate for DDT devices. Proceedings of 7th International Pyrotechnic Seminar, July 1980, Colorado, 1980, pp. 322-55.

4. Fronabarger, J.W. & Lieberman., M.L. Performance of chemical analogs of the explosive CP. Proceedings of 11th Symposium on Explosives and Pyrotechnics. 1981, Philadelphia, 1981, pp.38-1 to 38-14.

5. Tomlinson, W.R.; Ottoson, K.G. & Audriete, L.F. Explosive properties of metal amines. J. Am. Chem. Soc., 1949, 71,375-76.

6. Joyner, T.B. Explosive sensitivity of cobalt (III) complexes. Can. J. Chem., 1969, 47, 2729-30.

7. Belyaev, A.F.; Bobolev, V.K.; Korotkov, A.I.; Sulimov, A.A. & Chuiko, S.V. Deflagration-to-detonation transition in solid system. Nauka, Moscow, 1973. p 292.

8. Fogelzang, A.E.; Egorshev, V.Yu; Sinditskii, V.P. & Dutov, M.D. Combustion of nitro derivatives of azidobenzenes and benzofuroxans. Combust.& Flame, 1991, 87, 123-35.

9. Grinberg, A.A. Introduction in chemistry of coordination compounds. Chimia, Leningrad, 1971. p 631.

10. Ivanov, V.G. & Savinov, G.L. Exothermic reactions of perchlorate hydrozinates of alkaline metals at dynamic conditions. Fizika Gorenia i Vzryva (Russ. J. Phys. Comb. Explosion), 1991, 27(4), 18-24.

11. Engineering Design Handbook-Explosives Series: Properties of explosives of military interest. The U.S. Army Material Command Pamphlet No 706-177, January 1971, pp.187-90.

12. Sinditskii, V.P.; Sokol, V.I.; Fogelzang, A.E.; Dutov, M.D.; Serushkin, V.V.; Porai-Koshits, M.A & Svetlov, B.S. Vibrational spectra and structure of coordination compound with 4-amino-1,2,4-triazole as the bidentate ligand. Zh.Neorg.Khimii (Russ. J. Inorg.Chem.), 1987, 32(8), 1650-55.

13. Sinditskii, V.P.; Sokol, V.I.; Fogelzang, A.E.; Dutov, M.D.; Serushkin, V.V. & Porai-Koshits, M.A. Structure of coordination compound of metals with 4-amino-1,2,4 triazole as the monodentate ligand. Zh.Neorg.Khimii (Russ. J. Inorg.Chem.), 1987, 32(11), 2726-29.

14. Fogelzang, A.E.; Egorshev, V.Yu; Sinditskii, V.P.; Serushkin, V.V. & Saklanty, A.R. Study of burning behaviour of chemical analogs of explosive CP. Proceedings of 18th International Pyrotechnics Seminar, 1992, Colorado, 1992, p.303- 20.

15. Sinditskii, V.P.; Dutov, M.D.; Sokol, V.I.; Fogelzang, A.E. & Serushkin, V.V. Synthesis and investigation of structure of coordinating compounds with oxalylbisamidrazone. *Zh.Neorg.Khimii (Russ. J. Inorg.Chem.)*, 1990, **35**(12), 3124-30.

16. Sinditskii, V.P.; Fogelzang, A.E.; Dutov, M.D.; Serushkin, V.V.; Yarkov, S.P.; Svetlov, B.S. & Porai-Koshits, M.A. Complexes of carbohydrazide with copper(II) salts. *Zh.Neorg.Khimii (Russ. J. Inorg.Chem.)*, 1986, **31**(7), 1759-65.

17. Sinditskii, V.P.; Fogelzang, A.E.; Dutov, M.D.; Sokol, V.I.; Serushkin, V.V.; Svetlov, B.S. & Porai-Koshits, M.A. Structure of metal chloride, sulfate, nitrate and perchlorate complexes with carbohydrazide. *Zh.Neorg.Khimii (Russ. J. Inorg. Chem.)*, 1987, **32**(8), 1944-49.

18. Sinditskii, V.P.; Dutov, M.D.; Fogelzang, A.E.; Vernidub, T.Ya; Sokol, V.I. & Porai-Koshits, M.A. Synthesis and spectroscopic studies on nickel(II), cobalt(II) and copper(II) complexes of tetrazolyl-l-acethydrazide. *Inorg. Chim. Acta*, 1991, **189**, 259-66.

19. Sinditskii, V.P.; Sokol, V.I.; Dutov, M.D. & Fogelzang, A.E. Complexes of tetrazolyl- I-acethydrazide with lead salts. *Zh. Neorg. Khimii (Russ. J. Inorg.Chem.)*, 1990, **35**(9), 2224-28.

20. Fogelzang, A.E.; Adzhemian, V.Ja. & Svetlov, B.S. The influence of oxidizer nature in explosives on the burning rate. *Dokl. Akad. Nauk SSSR*, 1971, **199**(6), 1296-98.

21. Gorbunov. V.V. & Shmagin. L.F. Copper tetramine salts burning, *Fizika gorenia i vzryva (Russ. J. Phys. Combust. Explosion)*, 1972, **8**(4), 523-26.

22. Sinditskii, V.P.; Fogelzang, A.E.; Dutova T.Ya & Egorshev, V.Yu The catalytic behaviour of chemically bonded metals in the combustion of energetic materials containing various oxidizers. In Combustion, detonation, shock waves edited by S.M.

Frolov, Proceedings of Zeldovich Memorial, September 1994, Vol.2, Moscow, 1994, p.66-69.

23. Fogelzang, A.E.; Sinditskii, V.P.; Egorshev, V.Yu & Serushkin, V.V. Effect of structure of energetic materials on burning rate. In Decomposition, combustion and detonation chemistry of energetic materials. Edited by T.B. Brill, T.P. Russell, W.C. Tao, & R.B. Wardle. MRS symposium proceedings, November 1995, Boston, Vol. 418. Pittsburgh, 1996. p.151-61.

24. Latimer, V.M. The oxidation state of the elements and their potentials in aqueous solution, Prentice Hall, Englewood Cliffs, 1952.

25. Sinditskii, V.P.; Fogelzang, A.E.; Egorshev, V.Yu; Serushkin, V.V.; Dutov, M.D. & Dutova, T.Y. Catalysis and combustion mechanism of coordination compounds. Proceedings of 21st International Pyrotechnics Seminar, September 1995, Moscow, 1995, p.747-61.

26. Shuali, U.; Ottolenghi, M.; Rabani, J. & Yelin, Z. On the photochemistry of aqueous nitrate solution excited in the 195-nm band. *J. Phys. Chem.*, 1969, **73**(10), 3445-51.

27. Amichai, O. & Treinin, A. On the oxybromine radicals. *J. Phys. Chem.*, 1970, **74**(20), 3670-74.

28. Treinin, A. & Hayon, E. Absorption spectra and reaction kinetics of NO_2, N_2O_3 and N_2O_4 in aqueous solution. *J. Amer. Chem. Soc.*, 1970, **92**(20), 5821-28.

29. Moiseev, I.I. & Vergaftic, M.N. Metal-complex catalysis of oxidative reactions: principles and problems. *Yspekhi khimii (Russ. Chem. Rev.)*, 1990, **39**(12), 1931-59.

30. Collman, J.P.; Brauman, J.I. & Meunier, B. Epoxidation of olefine by cytochrome P-450 model compounds. *J. Am. Chem. Soc.*, 1985, **107**(7), 2000-05.

31. Groves, J.T.; Hausshalter, R.C.; Nakamura, M.; Nemo, T.E. & Evans, B.J. Hydroxylation and epoxidation catalyzed by iron- porphirine complexes. *J. Am. Chem Soc.*, 1979, **101**, 1032.

32. Muzart, J. Chromium catalyzed oxidation in organic synthesis. *Chem.Rev.*, 1992, **92**, 113-40.

33. Sheldon, R. A. & Kochi, J.K. Metal-catalyzed oxidation of organic compounds. Academic Press, NewYork, 1981. 423p.

34. Jatsimirskii, K.B. Redox properties of macrocyclic complexes of transition metals. *Teoret. eksp. khimia (Russ. Theor & Exptl. Chem.),* 1986, **3**, 280-85.

35. Preckel, R.F. Plateau ballistics in nitrocellulose propellants. *AIAA J.,* 1965, **3**, 346.

36. Lengelle, G.; Bizot, A.; Duterque, J. & Trubert, J.F. Steady- state burning of homogeneous propellant. In Fundamentals of solid-propellant combustion: Progress in Astronautics and Aeronautics, Vol.90, edited by M. Summerfield. AIAA. 1984. pp. 361-407

37. Singh, H. & Rao, K.R.K. Mechanism of combustion of catalyzed double base propellant. *Combust. Flame,* 1988, 71(2), 205-13.