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Review

Explosive Coordination Materials: Acyclic Ligands – Review

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Abstract: Coordination explosives form a significant group of energetic materials, which are mainly considered as novel primary explosives. Due to their modular structure, these compounds offer many possibilities for modifying their physicochemical and energetic properties. In this review the properties of complexes containing molecules such as ammonia, hydrazine, ethylenediamine, carbohydrazide, and guanidine derivatives are presented. The types of ligands and their influence on the physicochemical properties and detonation parameters are discussed.

Keywords: coordination compounds, energetic materials, explosives, complexes

Nomenclature

AN	Ammonium nitrate(V), NH_4NO_3
ANQ	1-Amino-3-nitroguanidine
AP	Ammonium chlorate(VII), NH_4ClO_4
CCP	see KKP
CHZ	Carbohydrazide, 1,3-Diaminourea, $OC(N_2H_3)_2$
CoHN	Trihydrazinecobalt(III) nitrate(V)

EN Ethylenediamine, $NH_2CH_2CH_2NH_2$
FCP Tris(carbohydrazide)iron(II) chlorate(VII)
KKP Tris(carbohydrazide)cadmium(II) chlorate(VII)
NCP Tris(carbohydrazide)nickel(II) chlorate(VII)
NHN Trihydrazinenickel(II) nitrate(V)
TACN Tetraaminecopper(II) nitrate(V), $[Cu(NH_3)_4](NO_3)_2$
TACuC Tetraaminecopper(II) chlorate(V)
TACuP Tetraaminecopper(II) chlorate(VII)

1 Introduction

The first coordination compounds were obtained in the nineteenth century, however in the beginning they were thought to be salts. Research on the preparation of low-toxicity primary explosives accelerated the development in this field [1].

Complexes consist of a central atom (metal cation), ligands, and acid anions [1-5]. The metal cation determines the structure of the compound and the number of ligands. It also often affects the sensitivity to mechanical stimuli. The ligand units serve as fuel due to the strongly negative oxygen balance (*e.g.* ammonia, hydrazine, 4-amino-1,2,4-triazole), but may also contain explosophoric groups (*e.g.* 5-nitrotetrazole). Regarding the amount of energy stored in the structure, high nitrogen ligands, such as triazole or tetrazole derivatives, are the most preferred. Anions of the acids, which are frequently NO_3^- and ClO_4^-, improve the oxygen balance and the heat of explosion. They can also increase the sensitivity to mechanical stimuli (*e.g.* azides). The chemical stability of complexes is determined by the strength of the coordination bonds, which depends on the type of ligands and the metal cation.

Coordination explosives are applied in a wide range of applications. The complexes decompose into the elemental metal or metal oxide, which can catalyze the burning process of propellants. They can serve as components of pyrotechnic compositions and as gas generants. Coordination primary explosives are less sensitive to mechanical stimuli, have higher thermal and chemical stability, and lower toxicity than classical primaries. They are safer in production, transportation, and use, and can be initiated by laser radiation. This is why they are considered as promising ingredients.

This article describes the characteristics of coordination explosives with regard to the type of ligand. Compounds that contain only noncyclic ligands in their structure are discussed. Also, information concerning their sensitivity, detonation parameters, physicochemical properties, and synthesis is presented.

2 Coordination Explosives with non-Cyclic Ligands

2.1 Coordination explosives with ammonia

Ammonia is the simplest ligand that may be present in energetic complex compounds. It has a free electron pair on the nitrogen atom, which can create a coordination bond with the metal cation. Historically [6] the first coordination explosive contained ammonia and was described in 1585 by the German alchemist Sebald Schwaertzer. It was called fulminating gold and it was the product of the reaction between gold(III) compounds and aqueous ammonia solution. Steinhauser *et al.* [6] noted that not all synthetic methods led to the same product, and the use of different amounts of ammonia affects the variable ratio of Au, N, H, and Cl in the structure. Fulminating gold is very sensitive to friction and flame. It decomposes explosively at 210 °C.

Another ammonia complex is tetraaminecopper(II) nitrate(V) $[Cu(NH_3)_4](NO_3)_2$ (TACN), Figure 1 [7-12]. This compound has a high impact sensitivity (4 J) and a small critical diameter (<4 mm). In a steel pipe it detonates with a velocity of 3498 m/s at 0.87 g/cm^3. Experimental detonation parameters at 0.9 g/cm^3 gave a heat of detonation (2970 kJ/kg), velocity of detonation (3177 m/s) and pressure of detonation (3.53 GPa) similar to calculated values (3176 kJ/kg, 3422 m/s, 2.72 Gpa, respectively). This complex was studied by Kunzel *et al.* [8] as an additive to ammonium nitrate (AN) to enable detonation in a small diameter. It was estimated that a composition containing 16% TACN and 84% AN (0.91 g/cm^3, 1480 m/s) detonates in a steel tube with a diameter of 2 mm. That means that the addition of the complex increases the sensitivity to a shock wave and allows the use of a smaller detonator.

Tetraaminecopper(II) chlorate(V) (TACuC), Figure 1(a)) is a primary explosive with high sensitivity to impact (3 J) [12]. It detonates with a velocity of 4300 m/s and deflagrates after ignition. Disadvantages of TACuC are both its slow decomposition during storage and lack water resistance. An analogue of TACuC is TACuP – tetraaminecopper(II) chlorate(VII) (Figure 1(b)) [13, 14]. This is a secondary explosive with a lower sensitivity than TACuC. TACuP decomposes at 243 °C. Its critical diameter, determined in a cone and telescopic charge, is 3 mm and its critical layer is also low (3 mm). The brisance is similar to TNT, which means that it is a strong explosive. The compound burns quickly with a bright blue flame and its deflagration can transition to detonation. It is not resistant to water and it can hydrolyse.

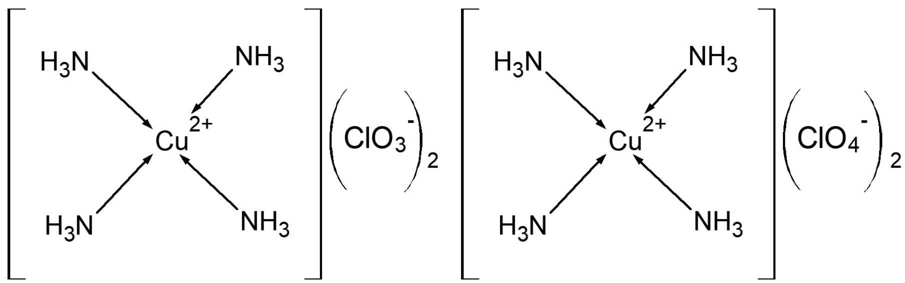


Figure 1. Ammonia complexes: TACuC (a) and TACuP (b)

The literature also contains some information on Co complexes with NH_3 and ClO_3^-, ClO_4^-, IO_3^-, MnO_4^-, and BO_3^{3-} anions [12, 15-19]. These materials are characterized by high impact sensitivity and low thermal stability. Unfortunately, the literature lacks information about other explosives with NH_3 as a ligand. These materials, due to their high sensitivity, have been little tested.

2.2 Coordination explosives with hydrazine

Another common noncyclic ligand is hydrazine, a strong reducing agent, an inorganic compound built of two nitrogen and four hydrogen atoms. The presence of free electron pairs on the nitrogen atoms enables the formation of bidentate compounds and coordination polymers. The most important member of this group is trihydrazinenickel(II) nitrate(V) (NHN) [20-23]. NHN is a coordination polymer in which Ni cations, hydrazine molecules and NO_3^- anions form a hexagonal crystal structure [20-23]. Its explosive parameters are as follows:

– velocity of detonation 7000 m/s at density 1.7 g/cm^3,
– detonation pressure 20.8 GPa, and heat of explosion 4200 kJ/kg [20-26],
– charges with a density of 0.8 g/cm^3 detonate with a velocity of 4300 m/s,
– its sensitivity to mechanical stimuli is equal to 10 J for impact, 24 N for friction, and 0.02 J for electric spark [23].

NHN decomposes at 218 °C. NHN is resistant to atmospheric oxygen, solar radiation, and to 48 h of exposure to UV radiation (366 nm). It explodes in the presence of concentrated acids. This material has a good ability to perform work in the underwater test, which is estimated at 100% TNT and 75% 2,2-bis(nitratomethyl)propane-1,3-diyl dinitrate (PETN). Pressed to 1.6 g/cm^3, it detonates from the fire impulse of a powder fuse and an electric ignition head. About 250 mg can initiate PETN pressed in an aluminum shell. Its initiating ability is better than the currently used primary materials. NHN can be used as a single explosive and also in mixtures with $KClO_3$, $Pb_2[Fe(CN)_6]$, AgN_3 or with glass [23]. NHN is definitely a stronger primary explosive than lead(II) azide (LA) [22]. Furthermore, it is less sensitive to mechanical stimuli and electric spark.

Another important coordination compound is trihydrazinecobalt(III) nitrate(V) (CoHN) [26]. It has a low sensitivity to impact (>25 J) and a high sensitivity to friction (60 N), and the least sensitive to electric spark (2.25 J) amongst the hydrazine complexes with NO_3^- anions. Addition of 25% water reduces its impact sensitivity. It explodes on contact with concentrated acids and decomposes slowly even in the presence of small amounts of water. CoHN decomposes thermally at 188 °C, has no initiating properties and is classified as a secondary explosive. The material can be used alone or in explosive compositions and propellants as a burning rate modifier.

In addition to the Ni and Co complexes, compounds with Cd, Zn, Fe, Mn, and Cr have also been obtained [24, 27]. These materials do not dissolve in water or other solvents. Their decomposition is rapid. The Zn complex decomposes at a very high temperature (310 °C), it is insensitive to friction and impact, but it is sensitive to electric spark. An analogous Mn complex decomposes at 150 °C and is insensitive to friction.

An example of an azide complex may be dihydrazinenickel(II) azide [28]. It is a primary material; 50 mg can initiate throughout to detonation a 1,3,5-trinitro-1,3,5-triazinane (RDX) charge. Its sensitivity to impact and friction is high (4.0 J, 72% of explosions at friction 10 N). It decomposes above 165 °C. Except for the Ni complex, azide complexes with the Co, Zn, and Mg analogues were also obtained. All of these materials have decomposition temperatures higher than 200 °C and they are characterized by lower sensitivities to impact than NHN.

Complexes with the ClO_4^- anion have high sensitivities to mechanical stimuli, except for the Zn complex (>25 J). The Cu analogue detonates during drying after synthesis at ambient temperature. The Ni complex can detonate when contacted by a baguetten in solution.

2.3 Coordination explosives with ethylenediamine (EN)

EN is a bidentate ligand, which creates five-membered rings or coordination polymers with metals [24]. A number of coordination explosives have been obtained, in which EN was the ligand, and the anions were NO_3^-, ClO_4^-, N_3^- and IO_3^-. Complexes with the NO_3^- anion are characterized by a very low impact sensitivity (>25 J) and a relatively high sensitivity to friction, similar to PETN. The chromium derivative ($[Cr(EN)_3](NO_3)_3$) can be considered as a low-sensitivity material. The thermal stability of EN complexes and the activation energy for thermal decomposition increases in the order: Cu < Co < Ni < Zn. The Cu complex $[Cu(EN)_2](NO_3)_2$ is characterized by a very quick transition from burning to detonation. Its detonation velocity is estimated as 8100 m/s at 1.97 g/cm^3 [24, 29]. Tris(ethylenediamine)nickel(II) nitrate(V), with the formula $Ni(EN)_3(NO_3)_2$, occurs in the form of cylindrical crystals with a deep blue colour. It decomposes at 262 °C.

The EN complexes were tested in a propellant composition with ammonium perchlorate (AP) and HTPB (3:1) as linear burning rate modifiers [29]. Each of the compounds tested caused an increase in the burning rate of the propellant. The largest increase was recorded for the Cu and Co complexes.

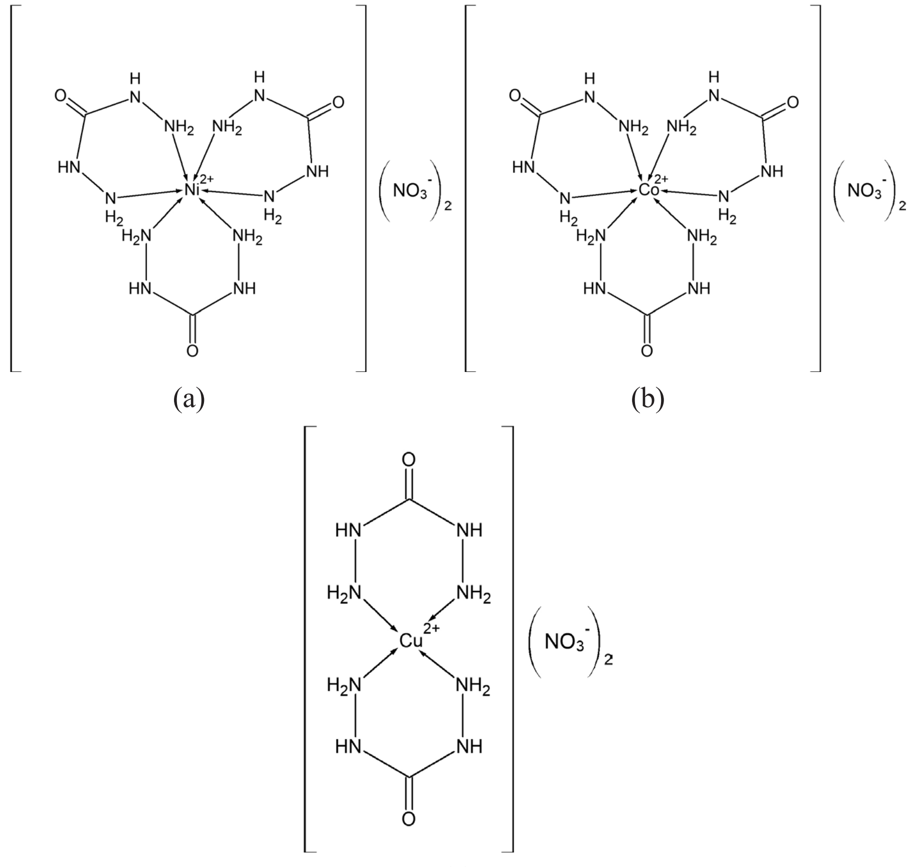
One of the most important compounds with the ClO_4^- anion is $[Cu(EN)_2](ClO_4)_2$ [24, 30]. This complex is sensitive to heat and explodes in contact with flame. It has relatively high detonation parameters and is characterized by a good ability to perform work in the underwater test, at the level of 110% TNT and about 75% PETN.

Complexes with other cations based on NO_3^- and ClO_4^- anions have similar parameters. An interesting compound is the cadmium complex with the N_3^- anion $[Cd(EN)(N_3)_2]_n$ [31]. It is a coordination polymer obtained from an aqueous solution of $Cd(NO_3)_2$, EN, and NaN_3, in 45% yield. The material decomposes at 265 °C, however decomposition commences in the range 200-210 °C. It is sensitive to impact.

2.4 Coordination explosives with carbohydrazide (CHZ)

CHZ has five possible places for coordination with free electron pairs – four places on nitrogen and one on the oxygen atom. The electrons of the carbonyl group are in resonance with the imino groups, therefore they participate less in the formation of a coordination bond with the central atom. CHZ can form four-, five-, and six-membered rings with metal cations [32-40]. These complexes attract the attention of researchers due to their high nitrogen content.

Ni (CNiN) and Co (CCoN) complexes (Figure 2) were obtained in the reactions between the metal nitrates(V) and CHZ, in a ratio of 1:3. The Cu complex (CCuN) (Figure 2(c)) was obtained from $Cu(NO_3)_2$ and CHZ (1:2) in an aqueous environment by precipitation with ethyl alcohol, in a yield exceeding 95% [32-35]. The sensitivities to impact and friction of these complexes are quite low. The compounds are stable up to 160 °C (CCoN), 220 °C (CNiN), and 75 °C (CCuN), and rapidly decompose at 276, 298 and 170 °C, respectively. The Co and Ni complexes increase the burning rate of propellants based on AP and HTPB [32].



(a) (b) (c)

Figure 2. CHZ complexes with NO_3^- anions: CNiN (a), CCoN (b) and CCuN (c)

Many compounds based on CHZ and the ClO_4^- anion have been synthesized and tested [32-40]. They have great thermal stability, high detonation parameters, and they are considered as promising primary explosives. Tris(carbohydrazide) cadmium(II) chlorate(VII) (KKP/CCP) and its Ni and Fe analogues, tris(carbohydrazide)nickel(II) chlorate(VII) (NCP) and tris(carbohydrazide) iron(II) chlorate(VII) (FCP), are very interesting materials. KKP is a primary explosive, it is characterized by a low sensitivity to impact (12 J) and a high sensitivity to friction (10 N) [27, 33]. It is several times less sensitive to mechanical stimuli than the currently used primaries. The minimum amount of KKP needed to stimulate RDX is 80 mg, and for PETN it is 200 mg. It has the highest temperature of decomposition (276 °C) among these complexes. Due to the relatively low sensitivity, high thermal stability, and a simple method of synthesis, it was used as a primary charge in an electric igniter to resist accidental initiation. Fe as the central atom coordinates three CHZ molecules [38]. It decomposes at 161 °C and is extremely sensitive to friction, impact and electric spark. Explosion can occur during filtration. The Co (CoCP) and Ni complexes are also primary materials [1, 32-35]. They have very high sensitivities to impact (1 J) and friction (≤5 N), and decompose at temperatures above 200 °C: 273 °C (NCP) and 243 °C (CoCP).

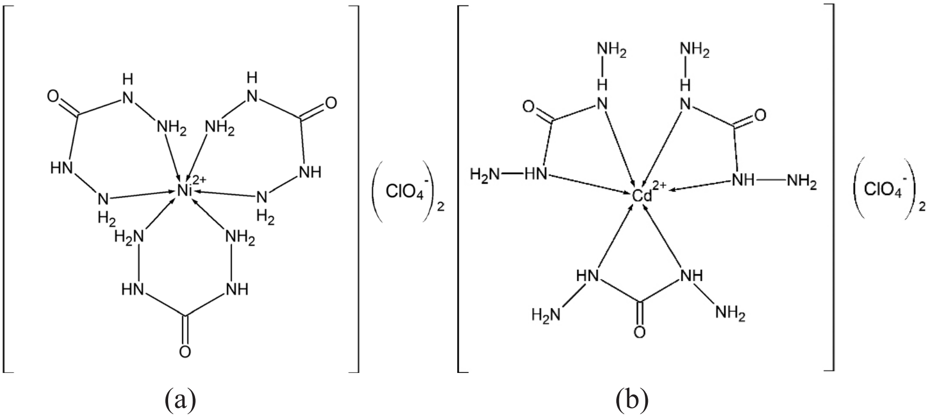


Figure 3. CHZ complexes with ClO_4^- anions: NCP (a) and KKP (b)

The Cu complex with the ClO_4^- anion is a very sensitive material (3 J, <5 N), with low thermal stability. It has a different structure to the other compounds – the Cu cation coordinates only two ligands. The Zn complex (ZnCP) decomposes in two stages with 67% weight loss [36]. It is characterized by a very high sensitivity to mechanical stimuli: 1.5 J and 20 N. In the cases of MnCP and MgCP, sensitivity is on a similar level, and the decomposition temperatures are slightly lower than that for ZnCP [39]. The properties of these complexes were collected in Table 1.

Table 1. Properties of some CHZ complexes

Parameter	Complex						
	CuCP	NCP	KKP	CoCP	ZnCP	MgCP	MnCP
Impact sensitivity [J]	3.0	1.0	12.0	1.0	1.5	2.5	2.0
Friction sensitivity [N]	<5	≤5	10	≤5	20	60	24
Electrostatic discharge sensitivity [J]	0.020	0.300	0.120	0.035	0.700	0.200	0.500
Decomposition temperature [°C]	186.0	273.0	275.5	243.0	268.0	239.0	263.0

NCP and CoCP stimulate tetrile in the igniter to detonation, but ZnCP has no initiating ability. NiCP, CoCP, and CuCP are sensitive to laser radiation (940 nm). KKP is the most promising CHZ complex. Its sensitivity to mechanical stimuli is low in relation to the currently used primary explosives. Due to its high thermal stability this material was used in igniters to resist accidental initiation. Despite their high sensitivity, NCP and CoCP are proposed for gas generator applications. Other complexes are too sensitive, which precludes their use.

2.5 Coordination explosives with guanidine derivatives

Guanidine is an organic compound belonging to the imines group with strong basic properties. Nitroguanidine is the most popular guanidine derivative, and is an explosive widely used in so-called three-base gun powders [41].

Fischer *et al*. [35] obtained complexes with 1-amino-3-nitroguanidine (ANQ, **1** in Figure 4) and ClO_4^-, NO_3^-, Cl^-, and dinitramine anions. Materials **2-13** (Figure 4) were obtained as a result of the reaction between a salt of the respective metal and a hot aqueous ANQ solution. Compounds **12** and **13** with a dinitramine anion were obtained through anion exchange, by the addition of the dinitramine ammonium salt to the ClO_4^- complex solution. ANQ derivatives are normally sensitive to mechanical stimuli, while complexes **4**, **6**, **9,** and **11** are extremely sensitive to impact. These materials decompose above 100 °C; only four of them withstand heating above 200 °C. Compounds **2**, **4** and, **6** are sensitive to a single laser pulse (100 μs) with a wavelength of 940 nm.

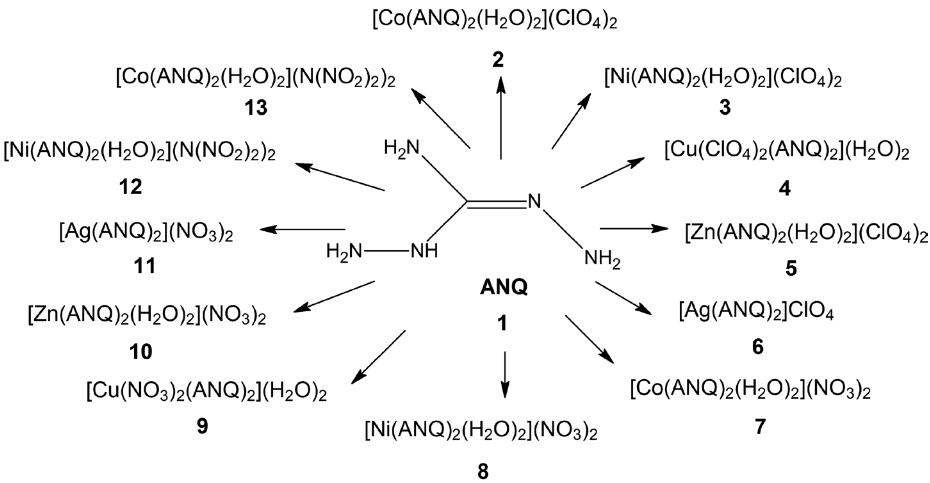
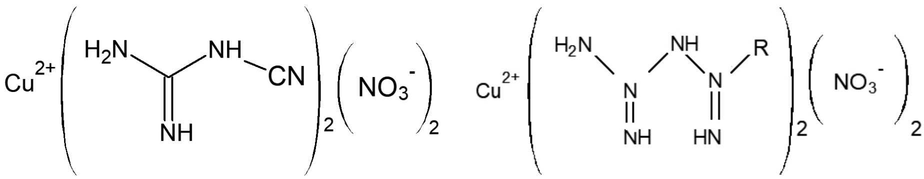


Figure 4. Formulas of 1-amino-3-nitroguanidine complexes

Jalovy *et al.* [42] obtained a number of coordination compounds with the Cu(II) cation and cyanoguanidine or 1-amidinoisourea. The formulas of these complexes are shown in Figure 5. They have higher thermal stabilities than the reference complex (172 °C). Bis(cyanoguanidine)copper(II) nitrate(V) was tested in gas generator compositions, however, its low decomposition temperature and low chemical stability excluded it from further studies [42]. Guanidine derivatives are not popular ligands. Only a few publications, with little information, can be found in the literature. Cyanoguanidine and 1-amidinoisourea complexes have been tested in pyrotechnic car safety systems [42-45],as possible replacements for NaN_3.



(a) (b)

Figure 5. Formulas of cyanoguanidine (a) and 1-amidinoisourea (b) complexes

3 Conclusions

- TACN detonates at a really high velocity. It has been added at 16% to AN in order to improve the detonation ability and to reduce the critical diameter. The other complexes are poorly studied.
- NHN is definitely one of the strongest primaries of the hydrazine complexes. Its detonation parameters are much higher and its sensitivity to mechanical stimuli and electric spark are lower than for lead(II) azide. Therefore, it is considered to be a future explosive.
- CoHN is classified as a secondary explosive. It can be used alone, in explosive compositions or in propellants as a burning rate modifier.
- The EN complexes could be linear burning rate modifiers, because they increase the burning rate of propellants. The highest increase was recorded for the copper and cobalt complexes.
- The most promising complexes are those based on the carbohydrazide ligand, especially KKP. It is a primary explosive, several times less sensitive to mechanical stimuli than the currently used primaries. KKP was used in an electric igniter resistant to accidental initiation.
- The presented complexes have the following advantages: simple synthesis,

low price, safety in use, production and transportation. As disadvantages we can point out quite high sensitivities and low decomposition temperatures.

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