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Review

Coordination Explosive Materials: Cyclic Ligands – A Review

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Abstract: Coordination explosives are a fairly well-studied group of explosives. They have possible widespread applications, such as initiation charges in initiation systems, components of pyrotechnic mixtures and gas generators, as well as propellant burn rate modifiers. There are many papers about these materials in literature, but there is a lack of review papers describing their properties. This review concerns complex explosives containing heterocyclic molecules with a five-membered ring in their structure. The compounds are characterized in terms of their physico-chemical and explosive properties depending on the substituted ligand.

Keywords: energetic materials, explosives, complexes, primaries, safety engineering

Nomenclature

1-MeHAtNO$_2$	1-Methyl-5-nitroimino-1*H*-tetrazole
2–MeHAtNO$_2$	2-Methyl-5-nitroamino-1*H*-tetrazole
4-AT	4-Amino-1,2,4-triazole
5-AT	5-Amino-1*H*-tetrazole
5-NT	5-Nitro-1*H*-tetrazole
AN	Ammonium nitrate(V), NH_4NO_3

ANTm	5-Amino-1-nitroso-1*H*-tetrazole
AZT	5,5'-Azobis(1*H*-tetrazole)
AP	Ammonium chlorate(VII), NH_4ClO_4
BMDTE	1,2-Bis(1-methyltetrazol-5-yl)ethane
BNCP	Di(5-nitrotetrazole-N2)teraaminacobalt(III) perchlorate
BNNP	Di(5-nitrotetrazole-N2)teraaminanickel(II) perchlorate, $[Ni(NT)_2(NH_3)_4]ClO_4$
BTA	*N*,*N*-Bis(1(2)-*H*-tetrazolato-N2)amine
CP	(5-Cyano-1*H*-tetrazolato-N2)pentaaminacobalt (III) dichlorate(VII)
Cutno	Aquadiaminacopper(II)4,4',5,5'-tetranitro-1,1'*H*-biimidazolate, $[Cu(TNBI)(NH_3)_2(H_2O)]$
DAT	1,5-Diamino-1*H*-tetrazole
DATr	3,4-Diamino-1,2,4-triazole
DTE	1,2-Bis(1*H*-tetrazol-2-yl)ethane
DTM	Bis(1*H*-tetrazol-5-yl) methane
DTP	2,2-Bis(1*H*-tetrazol-5-yl) propane
H_2AtNO_2	5-Nitroimino-1*H*-tetrazole
HAT	3-Hydrazine-4-amino-1,2,4-triazole
HN_5	1*H*-Pentazole
IMI	Imidazole
KKP	Tris(carbohydrazide)cadmium(II) chlorate(VII)
LA	Lead azide
NCAm	Nitrosocyanamide
NCP	Tris(carbohydrazide)nickel(II) chlorate(VII)
NT	5-Nitro-1*H*-tetrazole
NKT	Pentaamine(5-nitro-2*H*-tetrazolato-N2)cobalt (III) perchlorate
MNCuP	(5-Nitrotetrazole-N2)trisaminacopper(II) perchlorate, $[Cu(NT)(NH_3)_3]ClO_4$
MNZnP	(5-Nitrotetrazole-N2)trisaminazinc(II) perchlorate, $[Zn(NT)(NH_3)_3]ClO_4$
MTZ	1-Methyl-5*H*-tetrazole
PA	2,4,6-Trinitrophenyl
PETN	Pentaerythritol tetranitrate
RDX	1,3,5-Trinitro-1,3,5-triazine, hexogen
TATm	1,2,5-Triamine-1,2,3-triazole
TCuP	Poly[tris(4-Amino-1,2,4-triazole)copper(II)perchlorate], $\{[Cu(4\text{-}AT)_3](ClO_4)_2\}_n$
TNBI	4,4',5,5'-Tetranitro-1,1'*H*-biimidazole
TNR	2,4,6-Trinitroresorcinol
TNT	2,4,6-Trinitrotoluene

1 Introduction

Among the coordination explosives the most interesting are those containing high-nitrogen ligands. The most studied group of complexes are 1*H*-tetrazole and 1,2,4-triazole derivatives [1-17]. These materials have the best detonation parameters and high thermal stability. Among the 1*H*-tetrazole derivatives 5-nitro-1*H*-tetrazole, 5-cyano-1*H*-tetrazole and *N*,*N*-bis(1(2)-*H*-tetrazole)amine may be mentioned. High nitrogen content and positive enthalpy of formation gives high detonation parameters. These materials have comparable detonation parameters to typical explosives. By functionalizing the 1*H*-tetrazole molecule it is possible to modify their properties [7-16]. 1,2,4-Triazole derivatives, due to three donor nitrogen atoms in their structure, can form coordination polymers.

Obtaining complex explosives is quite a simple process and consists of 2-3 stages [2-16]. Most often it involves mixing together a metal salt solution and ligand or its salts solution with the optional addition of an acid whose anions will form a compound. An example of the synthesis of an explosive complex is shown in Figure 1.

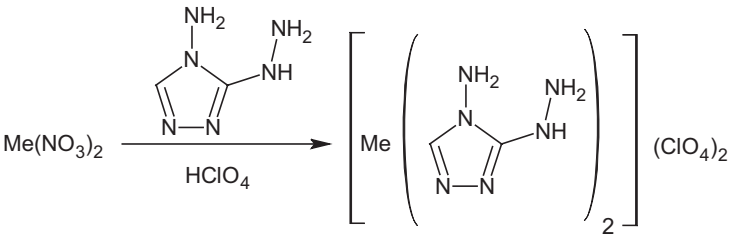


Figure 1. Scheme of synthesis of 3-hydrazine-4-amine-1,2,4-triazole complexes

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

Molecules of heterocyclic compounds and explosives can occur as ligands, and also as an anion because of the labile proton in their structures. Structural formulas of such materials and examples of these compound are presented in Figure 2.

$[M(L)_n](X)_m$ $[M(L)_n(Ex)_m]$ $[M(L)_n](Ex)_m$

Examples:

$[Ni(N_2H_4)_3](NO_3)_2$ $[Cu(NH_3)_2(BTA)]$ $[Co(NH_3)_5N_3](AZT)(H_2O)$

Figure 2. An example of building explosive complexes: M – central atom, L – ligand, X – anion and Ex – explosive

This article describes characteristics of complex explosives regarding the type of ligand. Compounds containing only heterocyclic ligands in their structure are discussed. Also, information about their sensitivity, detonation parameters, physico-chemical properties, and synthesis are presented.

2 Coordination Explosives with Heterocyclic Ligands

2.1 Coordination explosives with imidazole

Imidazole (IMI) is a heterocyclic compound containing two nitrogen atoms in its structure, of which nitrogen number three is combined with a metal cation by a coordination bond. IMI containing nitro, amino and azide groups are high energy compounds which have been widely studied [17, 18]. However, there is a lack of information in literature about their complex derivatives. The authors of [17] obtained IMI complexes with the formulas $[Co(IMI)_6](ClO_4)_2$, $[Cu(IMI)_4](ClO_4)_2$ and $[Zn(IMI)_4](ClO_4)_2$ (Figure 3). Materials are not stable below 200 °C and above 250 °C, they decompose. They are sensitive to heat, flame and mechanical stimuli. Copper and nickel compounds with an azide anion of formula $M(IMI)_4(N_3)_2$ are described in [18]. The copper complex is sensitive to impact and friction, but the nickel version has low sensitivity to mechanical stimuli and is sensitive to flame. Materials decompose at very high temperatures, but in the initial heating stage they canundergo endo- and exothermic transformations with low weight loss.

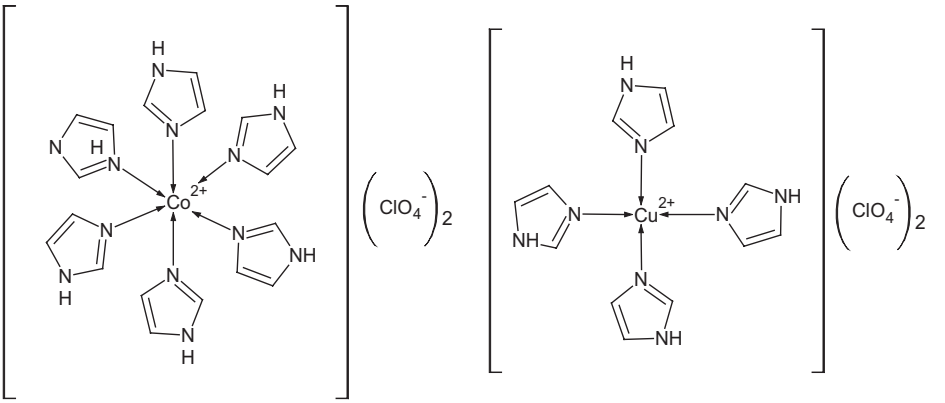


Figure 3. Structure of cobalt (left) and copper (right) imidazole complexes

An interesting compound containing an IMI derivative in its structure is CuTNO (Figure 4) [19-22]. This complex consists of a copper cation, ammonia and water molecules as ligands and 4,4',5,5'-tetranitro-1,1'*H*-biimidazole as an anion. The complex is characterized by quite low sensitivity to mechanical stimuli (6.5 J, >360 N). Material decomposed in one step at 198 °C. Detonation parameters calculated using Cheetah are at the TNT level, at 1.97 g/cm^3 the velocity of detonation being 7346 m/s, a detonation pressure of 23.44 GPa, with a heat of detonation of 3881 J/g. CuTNO has been tested as an energetic component In heterogenous propellant based on ammonium perchlorate and HTPB [22]. The addition of the complex reduced sensitivity to frictionand increased the hardness. CuTNO can be used as an energetic component in propellants and as a replacement for RDX or other explosives in compositions.

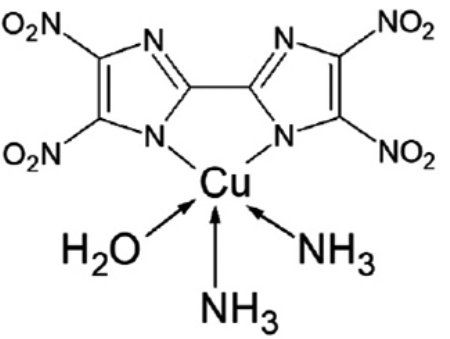


Figure 4. Structure of CuTNO

2.2 Coordination explosives with 1,2,4-triazole

Triazole is a heterocyclic compound, which exists in the form of four isomers: 1*H*-1,2,3-triazole, 2*H*-1,2,3-triazole, 1*H*-1,2,4-triazole and 4*H*-1,2,4-triazole. Triazole containing 60.84% nitrogen in structure, as well as its derivatives, is classified as a high-nitrogen compound. 1*H*-1,2,4-triazole derivatives are most commonly found in coordination explosives [1-6]. Three nitrogen atoms are electron pair donors, it being possible to create multi-core compounds in which a ligand molecule connects coordination atom. 1,2,4-Triazole is coordinated by the metal in positions 1 and 2 to create coordination polymers. It can combine through functional groups such as amino, nitro or hydrazine substituted to a carbon atom. This allows a wide range of modification properties of the complex compounds.

Complexes with 4-amino-1,2,4-triazole (4-AT) were first synthesized in the 1970s. 4-AT has a high nitrogen content (66.6%) and can form single, multi-core compounds and coordination polymers [1]. Cudziło and Nita [2] synthesized a copper complex $[Cu(4\text{-}AT)_4(ClO_4)(H_2O)](ClO_4)$ **(1)**. Under initial heating, the compound loses its water molecule at 115-150 °C, and at 160-170 °C the 4-AT molecule is disconnected, which transforms the material into the coordination polymer $\{[Cu(4\text{-}AT)_3](ClO_4)_2\}_n$, which decomposes explosively at 310.8 °C. Another material obtained by Cudziło and Nita [4] is a coordination polymer consisting of a copper cation, three chloride bridges, two 4-AT molecules and a chlorate(VII) anion **(2)** (Figure 5). The compound is stable up to 235 °C at which temperature it begins to slowly degrade up to 295 °C at which it rapidly decomposes. During friction sensitivity testing the complex gives 100% positive results at a force of 9.8 N. It is a primary explosive, which in charges amounting to 0.3 g ,stimulated by an ignition flame, initiated a PETN charge. It explodes even in a 1 mg charge. Charges at density of 1.80 g/cm^3 in dural tubes detonate at a velocity of 1900 m/s.

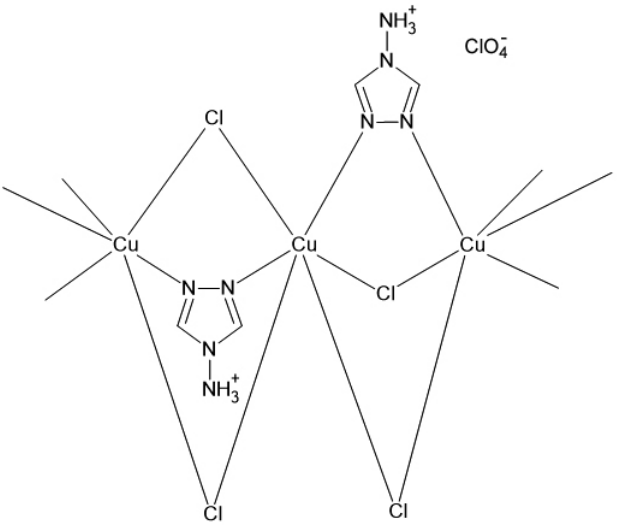


Figure 5. Structure of $\{[Cu(4\text{-}AT)_2Cl_3]ClO_4\}_n$

Another 4-AT coordination polymer is $\{[Cu(4\text{-}AT)_3](ClO_4)_2\}_n$ (TCuP, **(3)**), Figure 6 [5, 6]. It is a primary explosive which in charges of 200 mg stimulate PETN charge. It is characterized by a lower sensitivity to impact and friction (1 J and 10 N) than typical primaries. The complex is thermally stable up to 250 °C and decomposes at 310 °C. Detonation velocity at bulk density (1.4 g/cm^3) is 6500 m/s and the Gurney energy is 2160 (0.79 g/cm^3) and 2410 J/g (0.89 g/cm^3). In contact with flame, the compound detonated. The material can be used as a low-toxic replacement for lead azide (LA). $[Ag_2(C_2H_4N_4)_3(H_2O)](ClO_4)_2$ **(4)** [3] as another primary. The compound has a high density (2.46 g/cm^3) and is characterized by high sensitivity to impact and friction (2 J, 30 N). It decomposes above 240 °C. 0.3 g of the compound initiates 0.5 g of crystalline PETN and can be successfully used as a primary. Properties of the described complexes are in Table 1.

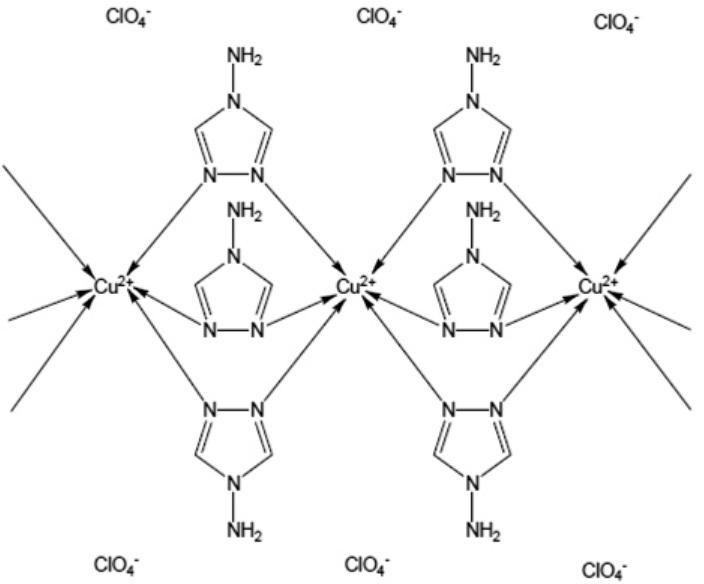


Figure 6. Structure of TCuP

Table 1. Properties of 4-AT complexes

Complex	**1**	**2**	**3**	**4**
Impact sensitivity [J]	5	–	1	2
Friction sensitivity [N]	50	–	10	30
Velocity of detonation [m/s] at density ([g/cm^3])	6610 (1.60)	1900 (1.80)	6500 (1.40)	–
Temperature of decomposition [°C]	–	295	310	>240

3,4-Diamino-1,2,4-triazole (DATr) has free electron pairs on the nitrogen atom in the 1,2,4-triazole ring and amino group, which allows coordination with the central ion [23]. DATr can be coordinated as a monodent ligand by the amino group, 1,2,4-triazole ring or it can be a bridging ligand by nitrogen atoms in position 1 and 2 in the ring. DATr complexes are hydrates, have high sensitivity to mechanical stimuli, are unstable at high temperatures, with the exception of compounds with chlorate(VII), which decompose in one step above 300 °C. Examples of DATr complexes are [24]:

– $Mn_3[(DATr)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$ **(1)**,
– $Co_3[(DATr)_6(H_2O)_6(NO_3)_6 \cdot 2H_2O$ **(2)**,
– $Ni_3[(DATr)_6(H_2O)_6](NO_3)_6 \cdot 1.5H_2O$ **(3)**, and
– $Zn_3[(DATr)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$ **(4)**.

These decompose in several stages above 260 °C with loss of the water molecule and phase changes. The most thermally stable compound is **(2)**, with the least being **(4)**. Complexes **(1)**, **(3)** and **(4)** are insensitive to friction, while **(2)** is the most sensitive. Compounds with a chlorate anion (VII) in the formula:

– $[Mn_5(DAT)_{12}(H_2O)_6](ClO_4)_{10}$ **(5)**,
– $[Co_5(DAT)_{12}(H_2O)_6](ClO_4)_{10}$ **(6)**,
– $[Ni_5(DAT)_{12}(H_2O)_6](ClO_4)_{10}$ **(7)**, and
– $[Zn_5(DAT)_{14}(H_2O)_2](ClO_4)_{10}\cdot 2H_2O$ **(8)**

are thermally stable, decompose in one step above 300 °C [24]. That with the lowest decomposition temperature has a cobalt complex **(6)** (328.6 °C), the highest has a nickel complex **7** (361.9 °C). The increase in thermal stability follows the sequence: **(6)** < **(5)** < **(8)** < **(7)**. Complexes **(6)** and **(7)** are very sensitive to impact and friction, while **(5)** and **(8)** are insensitive to impact and moderately sensitive to friction. Complex **(8)** is the least sensitive compound.

3-Hydrazine-4-amino-1,2,4-triazole (HAT) is a ligand with the highest nitrogen content (73.65%) among the ligands with the 1,2,4-triazole ring [7, 8, 25]. It connects to the coordination centre through nitrogen atoms from the ring and the terminal group $–NH_2$ from the hydrazine group. HAT with Cu, Ni, Co, Cd and chlorate(VII) anion create complexes sensitive to laser radiation [8]. The ability to be initiated by a laser depends on the oxidizing capacity of the metal ion. The higher this value, the stronger the oxidizing properties of the metal and the greater the sensitivity of the compound to laser radiation, which follows: Cu > Cd > Ni > Co. Materials have fairly good thermal stability, they decompose above 230 °C, except the copper complex, which decomposes in one step [8]. A very interesting compound is $[Cu(HAT)_2](ClO_4)_2$ which has a low laser initiation threshold, Figure 7. The material is very sensitive to mechanical stimuli with its sensitivity being similar to LA. To improve its safe working, the complex is phlegmatized with a PVMT polymer (10%) which reduces sensitivity. The minimum amount of complex required to initiate an RDX charge in a No 8 igniter tube is 0.025-0.030 g. This compound does not contain heavy metals and is sensitive to laser radiation even in phlegmatized form, so it can be a replacement for typical primaries.

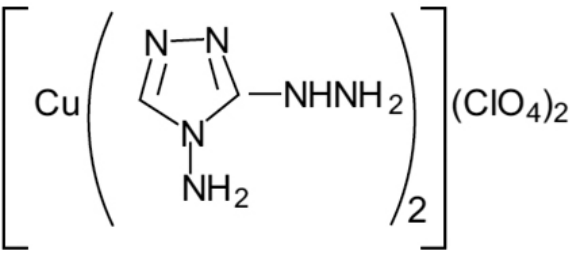


Figure 7. Structure of $[Cu(HAT)_2](ClO_4)_2$

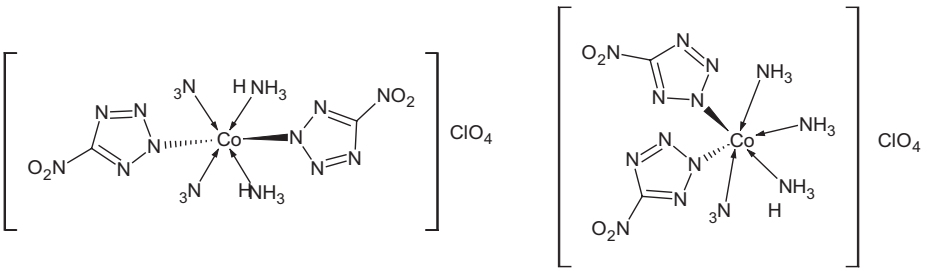
2.3 Coordination explosives with 1*H*-tetrazole

1*H*-tetrazoles are the most popular heterocyclic compounds as high energetic ligands. They are made up of a five-membered ring formed by four nitrogen atoms and one carbon atom. Compounds based on 1*H*-tetrazole have been studied for a very long time as replacements for currently used explosives [9-16, 21, 28]. The presence of a weakly bound proton on nitrogen atom number 1 allows the structure of the compound to be modified, affecting its physico-chemical properties and explosive parameters. These properties were used in the design of new coordination explosives by modifying the functional group in the 1*H*-tetrazole ring. 1*H*-tetrazole derivatives have the highest nitrogen content in their structure of all heterocyclic ligands. This causes high enthalpy of formation, high detonation parameters and high values of heat of explosion.

5-Amino-1*H*-tetrazole (5-AT) is a planar molecule with one carbon atom in its structure and a high nitrogen content of 82.33% [29]. In the complexes 5-AT connects with the central atom through the ring nitrogen atoms from positions 2 and 3. Bełzowski and Wojewódka [30] have received a number of complex compounds containing in their structure 5-AT and nitrate(V) or chlorate(VII) anions. The sensitivity to mechanical stimuli and electric spark is comparable to PETN and RDX. The least sensitive complexes are $[Hg(5\text{-}AT)_2](NO_3)_2$, $[Cu(5\text{-}AT)_2](ClO_4)_2$ and $[Co(5\text{-}AT)_3](ClO_4)_3$. Copper, cobalt and nickel complexes with perchlorate and copper with nitrate, detonated in an aluminium tube, initiated by LA. $[Cu(5\text{-}AT)_2](ClO_4)_2$ in amounts of 200 mg, initiates to detonation a PETN charge in an aluminum tube. Compounds containing copper, nickel and cobalt cations are sensitive to laser radiation. In underwater explosion tests, the highest parameters are demonstrated by the complex $[Cu(5\text{-}AT)_2](ClO_4)_2$ whose maximum pressure value corresponds to that of TNT and 80% of RDX and PETN. 5-AT complexes are not stable materials; they are hygroscopic and can absorb water from the atmosphere and dissolve in it. The compounds are characterized by high sensitivity.

1,5-Diamino-1*H*-tetrazole (DAT) is a material with the highest nitrogen content (83.97%) of 1*H*-tetrazole. The compound is highly able to form intra- and intermolecular hydrogen bonds in coordination compounds which affect the high stability of its derivatives. DAT forms an additional five-membered ring with a metal cation through coordinated amino groups [31-34]. DAT create forms with an Fe, Cd, Zn, Co and Cu and perchlorate anion [31, 32]. Complexes with copper and iron have two ligand molecules and cadmium and zinc have six molecules of ligand. Iron and copper complexes are primaries, their sensitivity to impact and friction is high and they decompose at temperatures above 200 °C. $[Cd(DAT)_6](ClO_4)_2$ is very sensitive to mechanical stimuli. It decomposes at 243 °C with initial decomposition occurring already at 197 °C [32]. Complexes containing six ligand molecules have hydrogen bonds which causes the formation of layers and stable three-dimensional structures.

5-Nitro-1*H*-tetrazole (NT) derivatives are some of the most frequently studied explosives. The properties of NT in complexes caused that its derivatives are characterized by very good parameters [9-16, 21]. Di(5-nitrotetrazole-N2)teraaminacobalt(III) perchlorate (BNCP) was obtained by Bates in 1986 [17, 35, 36]. The compound consists of four ammonia molecules, two 5-nitro-1*H*-tetrazole anions and one chlorate(VII) anion. It can occur in two forms -cis and -trans, as shown on Figure 8.



trans - BNCP *cis* - BNCP

Figure 8. Formula of trans- and cis-BNCP

BNCP is considered one of the most important and strongest primaries from the group of coordination compounds [14-17, 21, 35-39]. The complex has a high theoretical velocity of detonation value of 8100 m/s at 1.97 g/cm^3. It is slightly more sensitive than CP, its impact sensitivity (H_{50}) being 6 J, to friction 30 N and to electric spark 5 J. It is stable to 270 °C after which it rapidly decomposes. Some BNCP properties are given in Table 2.

Table 2. Properties of BNCP

Parameter	Value
Impact sensitivity H_{50} [J]	6
Friction sensitivity [N]	30
Electrostatic discharge sensitivity [J]	5
Temperature of decomposition [°C]	270
Velocity of detonation [m/s] at density ([g/cm^3])	5700 (0.64)
Theoretical velocity of detonation [m/s] at density ([g/cm^3])	8100 (1.97)
Density [g/cm^3]	2.05

BNCP has a short transition time from burning (deflagration) to detonation (10 ms). Only 0.05 g of complex initiates the RDX charge. BNCP is proposed not only as a primary charge in fuses, but also as a secondary charge due to its high detonation parameters. It exceeds currently used primaries regarding detonation parameters, higher thermal stability, lower sensitivity and higher safety during operation. BNCP is proposed as a replacement for LA and other explosives used in initiation systems. The complex was tested as a primary charge in electric fuses with LA, NHN or NCP/KKP composition and tetryl/PETN [36]. All except the BNCP(150)/LA(200) and BNCP(150)/NHN(200) systems passed the tests. Negative tests were probably the result of a too low BNCP mass. Complexes of 5-nitrotetrazole with copper, nickel and zinc cations were also obtained [36]:

– $[Cu(NT)(NH_3)_3]ClO_4$ (MNCuP),
– $[Ni(NT)_2(NH_3)_4]ClO_4$ (BNNP),
– $[Zn(NT)(NH_3)_3]ClO_4$ (MNZnP).

These compounds have a very high decomposition temperature (above 260 °C), except MNZnP (120 °C). They are sensitive to friction (except MNZnP) and their impact sensitivity is relatively low. Their properties are shown in Table 3. Another interesting complex is pentaamine(5-nitro-2*H*-tetrazolato-N2)cobalt (III) perchlorate (NKT) [35]. It is a thermally stable compound which can be heating for 6 h at 200 °C in a hermetically sealed container. Its decomposition temperature is 265 °C. NKT tested in boreholes withstands temperatures conditions of up to 150 °C at 80 MPa even for 6 h. Critical diameter is 6.5 mm at a crystal density of 1.63 g/cm^3 with the measured velocity of detonation being 6650 m/s (1.61 g/cm^3).

Table 3. Some properties of 5-NT complexes [15]

Properties	BNNP	MNCuP	MNZnP
Impact sensitivity H_{50} [J]	6.0	6.0	7.2
Friction sensitivity [N]	30	48	140
Density [g/cm^3]	0.54	0.65	0.85
Temperature of decomposition [°C]	278	260	120

Ilyushin To eliminate hydrogen chloride from decomposition products, Ilyushin *et al.* [13, 14, 35] decided to replace the chlorate(VII) anion in the NKT with the 1,2-dinitroguanidine anion (Figure 9). The complex has less impact sensitivity than PETN and decomposes in several stages above 100 °C. The calculated velocity of detonation is about 8 km/s, while the experimental value is 6420 m/s (1.74 g/cm^3). Compared to NKT the complex has weaker detonation properties.

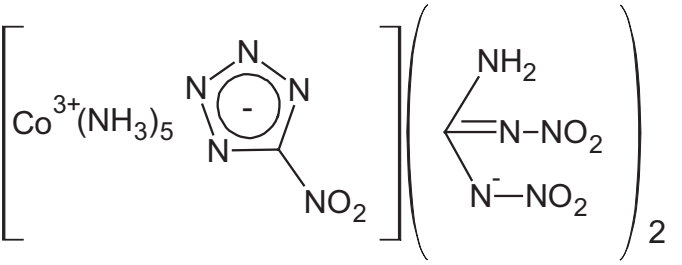


Figure 9. Formula of pentaamina(5-nitro-2*H*- tetrazolato-*N*2)cobalt(III) 1,2-diaminoguanidine

Meyer *et al.* [21, 35, 39] developed a new group of initiating compounds classified as so-called "green" explosives which do not contain toxic metals and chlorate anions. The complexes consist of iron(II) cation and 5-nitro-1*H*-tetrazole groups and water molecules as ligands. Four new anions were obtained with formulas: $[FeIINT_3]^-$, $[FeIINT_4]^{2-}$, $[FeIINT_5]^{3-}$, $[FeIINT_6]^{4-}$. As a cation were metal cation, ammonium, hydrazine, 1,2,5-triamine-1,2,3-triazole (TATm), nitrosocyanamide (NCAm) and 5-amino-1-nitroso-1*H*-tetrazole (ANTm) cations. Formulas of these complexes are shown in Figure 10. Compounds are stable up to 250 °C and insensitive to electric spark (Table 4). Compounds containing the sodium cation detonated in contact with flame, and in moisture form are insensitive to impact, friction and flame. Complexes do not show hygroscopicity, and do not decompose under the influence of moisture, light and heat.

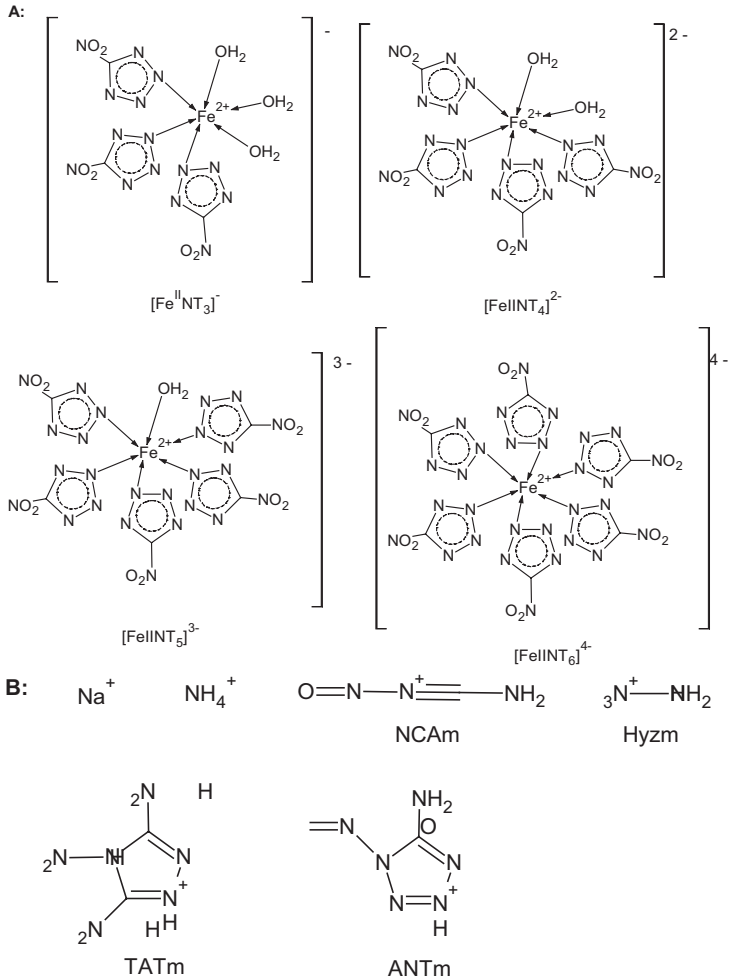


Figure 10. Formula of „green“ 5-nitro-1*H*-tetrazole complexes

Table 4. Properties of „green“ 5-nitro-1*H*-tetrazole complexes

Complex	Impact sensitivity [J]	Friction sensitivity [N]	Electrostatic discharge sensitivity [J]	Density [g/cm^3]	Temperature of decomposition [°C]
$NH_4[Fe^{II}NT_3]$	3.75	42	>0.36	2.10	261
$(NH_4)_2[Fe^{II}NT_4]$	3.00	28	>0.36	2.20	255
$(NH_4)_3[Fe^{II}NT_5]$	2.50	13	>0.36	2.34	253
$(NH_4)_4[Fe^{II}NT_6]$	2.00	8	>0.36	2.45	252

(5-Cyano-1*H*-tetrazolato-N2)pentaaminacobalt (III) dichlorate(VII) (CP) was obtained in 1968 in the USA as a potential replacement for extant primaries [21, 35, 40-46]. CP consists of a cobalt(II) cation, 5-cyano-1*H*-tetrazole, five ammonia molecules as ligands and two chlorate(VII) anions (Figure 11). The 5-cyano-1*H*-tetrazole ring connects with the cation *via* a nitrogen atom in position 2. This is the strongest bond that can be formed in a negatively charged ring and metal cation. CP is in the yellow monoclinic crystal form of 1.97 g/cm^3 density. The material decomposes at 290 °C. It is a primary which detonated at 7460 m/s (1.65 g/cm^3), detonation pressure of 17 GPa and heat of explosion of 4063 kJ/g. The loose form is characterized by a similar sensitivity as classic secondary explosives, however, when pressed is as sensitive as primaries which is considered an advantage. CP is compatible with most metallic and ceramic materials used in igniters, however, it cannot be used in contact with copper. Production of the complex began in 1977, and in 1979 the first fuse for the US Department of Energy was constructed. CP has been used as a primary explosive in "Spark-Safe Low-Voltage Detonators" and in safe low voltage electric igniters. Compared to commonly used materials, it has less sensitivity to mechanical stimuli (5 J) and is safer to use.

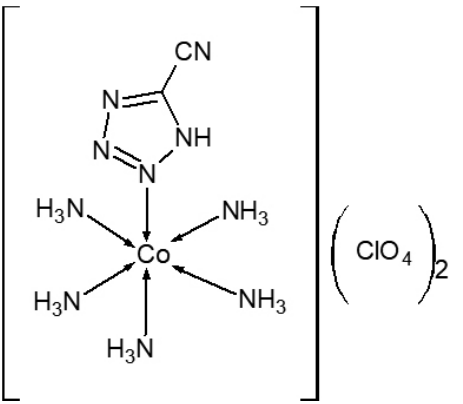


Figure 11. Structure of CP

There are many CP and BNCP analogues wich differ from each other's functional group in the 1*H*-tetrazole ring and metal cation. Fleming *et al.* [21, 35] obtained cobalt complexes with 5-substituted 1*H*-tetrazole functional groups as: –CN, –Cl, –H, –NO_2, –CH_3 and –CF_3 (Figure 12). These compounds are characterized by high densities in the range of 1.84-2.03 g/cm^3 and higher detonation parameters. They decompose above 250 °C, except for the 5-(1,2,3-trinitromethylene)-1*H*-tetrazole derivatives. Some properties are given in Table 5.

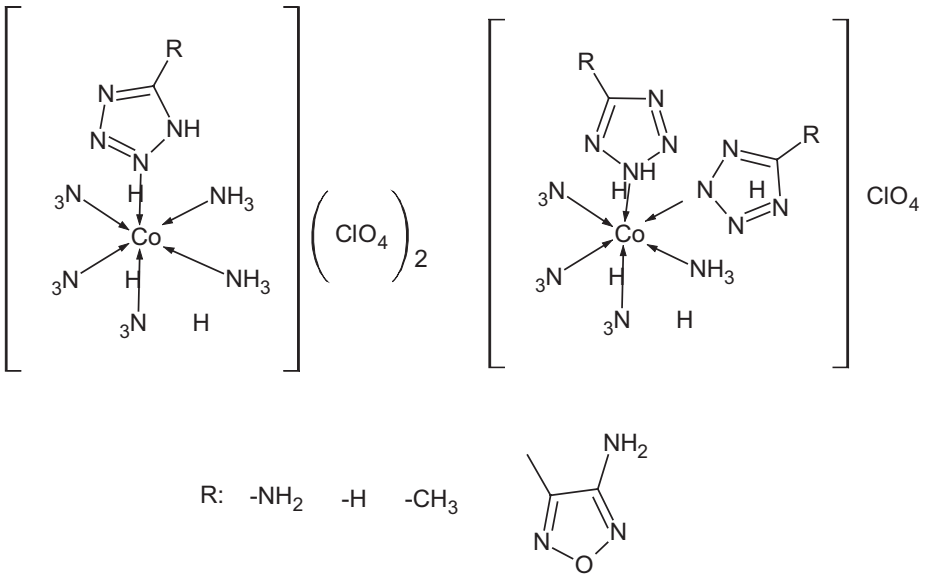


Figure 12. Structure of 5-substituted 1*H*-complexes

Table 5. Properties of 5-substituted 1*H*-complexes [21, 35]

Complex	Velocity of detonation [km/s] at density ([g/cm^3])	Theoretical velocity of detonation [km/s] at density ([g/cm^3])	Density [g/cm^3]	Temperature of decomposition [°C]
- H	–	7.14 (1.97)	1.97	280
- NO_2	6.65 (1.61)	6.30 (1.61)	2.03	265
- CH_3	–	6.94 (1.90)	1.88	282
- N–$NO_2^-NH_4^+$	6.33 (1.52)	–	1.87	250
- NH_2	6.50 (1.62)	6.14 (1.62)	1.95	270
- $C(NO_2)_2^-NH_4^+$	6.32 (1.48)	–	1.88	201
- CH_2N_3	–	7.44 (1.94)	1.94	302
- $C(NO_2)_3$	–	8.03 (2.05)	2.05	132
- nitrofurazane	–	7.76 (1.97)	1.97	280
- azydofurazane	–	7.71 (1.95)	1.95	198
- aminofurazane	–	7.34 (1.93)	1.93	280
- ammonium 4-nitramminefurazanylo	–	7.42 (1.83)	1.83	255

Another interesting group of complexes are compounds which have functional groups in the 1*H*-tetrazole ring, namely: amino, methyl and 3-nitrofurazan [21, 35]. Materials except 5-(3-nitrofurazanylo)-1*H*-tetrazole had a metal to ligand ratio of 2:3, the overall cation formula looks like $[Co_2(NH_3)_8(NT–R)_3]^{3+}$. One of the 1*H*-tetrazole rings forms a bridge between two metal cations by nitrogen atoms in positions 2 and 3, as shown in Figure 13. Analogues CP and BNCP with a 5 substituted 1*H*-tetrazole ring are characterized by good stability to high temperature and high theoretical detonation parameters. Materials containing 5-(aminofurazanylo)-1*H*-tetrazole, azide and 1,2-dinitroguanidine as anions, are primary explosives. Both compounds are characterized by very high theoretical detonation parameters and are less sensitive to impact than PETN.

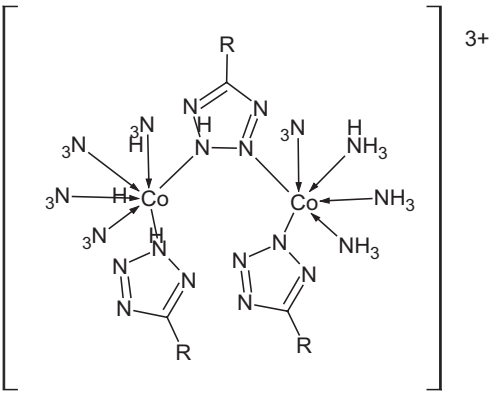


Figure 13. General formula of 5-substituted 1*H*-tetrazole complexes

5-Nitroimino-1*H*-tetrazole (H_2AtNO_2) connects to the metal cation via nitrogen atom in position 4 on 1*H*-tetrazole ring, but connections via one of the oxygen atoms from the nitro group are also known [47]. A number of energetic compounds were obtained with H_2AtNO_2 **(9)** and its methyl derivatives such as 1-methyl-5-nitroimino-1*H*-tetrazole (1-MeHAtNO2) **(10)** and 2-methyl-5-nitroamino-1*H*-tetrazole (2-MeHAtNO$_2$) **(11)** [48]. 5-Nitroimino-1*H*-tetrazole is a compound with sensitivity at the level of primaries (1 J, 8 N). Methyl derivatives are less sensitive compounds, especially those with a methyl group in the 2-position on the 1*H*-tetrazole ring. Sensitivity to mechanical stimuli of materials **(10)** and **(11)** are 12 J and 160 N and 30 J and 360 N, respectively. 2-Methyl-5-nitroimino-1*H*-tetrazole derivatives are characterized by high sensitivity, while those of 1-methyl-5-nitroimino-1*H*-tetrazole, with sensitivity similar to TNT. Derivatives of H2AtNO2 are low-sensitivity materials, the complexes having good thermal stability and which decompose above 200 °C.

Changing 5-nitroimino-1*H*-tetrazole and its derivatives into complex compounds contributed to a reduction of sensitivity to mechanical stimuli and thermal stabilization to 200 °C.

Complex compounds containing 1-methyl-5*H*-tetrazole (MTZ) as ligands in the structures were formed [49]. Obtained compounds containing chlorides, nitrates(V), chlorates(VII) as an anion and 2,4,6-trinitrophenyl (PA) and 2,4,6-trinitroreresin (TNR) and cations like: Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Ag^{+}. These complexes decompose above 200 °C, except those with a nitrate(V) anion. Most of these materials are unstable and undergo two-stage degradation as a result of loss of water or ligand molecules. Complexes with chloride and nitrate(V) anions are insensitive to mechanical stimuli. The addition of chlorate(VII) into the structure increases the sensitivity. These materials, due to the weak thermal stability and relatively high sensitivity to mechanical stimuli, will not find an application. A number of complexes based on bis(1*H*-tetrazol-5-yl) methane (DTM) and 1,2-bis(1*H*-tetrazol-2-yl)ethane (DTE) were obtained [50, 51]. The sensitivity to impact of DTM materials are very high, most of them are characterized by sensitivity at the single joule level. In the case of sensitivity to friction, the complexes have low sensitivity. Replacement of chloride and sulfate(VI) anion *via* nitrate(V) and chlorate(VII) anions increased the sensitivity to impact and friction of the complexes. The compounds decompose in several stages at temperatures lower than the DTM. Complexes with DTE and 1,2-bis(1-methyltetrazol-5-yl)ethane (BMDTE) were also synthesized [51]. Materials are sensitive to impact and very sensitive to friction. Complexes with (DTE) are more sensitive than those with DTM. Coordination compounds with 2,2-bis(1*H*-tetrazol-5-yl) propane (DTP) were also obtained [56]. The complexes were synthesized by reacting DTP with chlorates(VII), nitrates(V), chlorides and sulfates(VI) of the respective metals. Most of these compounds have a decomposition temperature close to or above that of DTP. Complexes with 2,2-bis(1*H*-tetrazol-5-yl) propane have quite good sensitivity, some of them being insensitive to mechanical stimuli.

A particularly interesting derivative of 1*H*-tetrazole is *N*,*N*-bis(1(2)-*H*-tetrazolato-*N*2)amine (BTA) [53-60]. The material is stable at high temperatures and begins to decompose above 250 °C. BTA creates coordination compounds with copper: $Cu(BTA)(NH_3)_2$ **(12)**, $Cu(BTA)(NH_3)_2 \cdot H_2O$ **(13)** and $(NH4)_2Cu(BTA)_2 \cdot 2.5H_2O$ **(14)** [53]. The synthesis of these materials consists of reacting BTA, copper chloride and ammonia in various molar ratios. $Cu(BTA)(NH_3)_2$ is a low-sensitivity material, during the sensitivity test it does not decompose at an impact of 40 J and friction of 360 N. It is a stable compound and decomposes above 295 °C. $[(NH_4)_2Cu(BTA)_2 \cdot 2.5H_2O]$, like compound

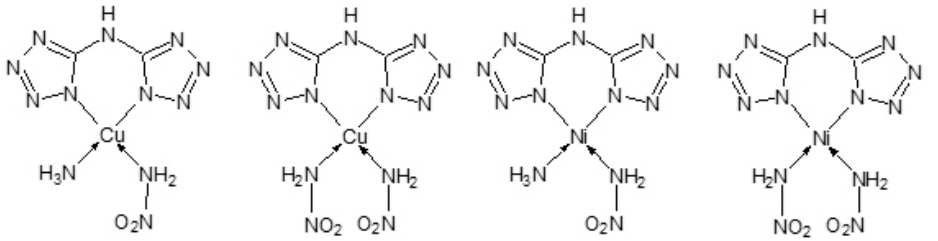
(12) is a non-sensitive material with high thermal stability (275 °C). It has two ammonium ligands coordinated by a copper cation and water molecules. The $[Cu(BTA)(NH_3)_2 \cdot H_2O]$ complex has not been tested due to the low synthesis yields ynthesis. Complexes **(12)** and **(14)** are interesting compounds and can be used as energetic components of pyrotechnic mixtures, explosive compositions, propellants, or gas generators. BTA complexes with lead cation $[Pb(BTA)(H_2O)]_n$ **(15)**, lead and copper cation (double coordination center) $[PbCu(BTA)_2(H_2O)_5] \cdot 2H_2O$ **(16)** and $PbCu(BTA))_2$ **(17)** [64]. Synthesis of complex **(15)** consisted of mixing aqueous solutions of lead nitrate and BTA and heating at 150 °C in an autoclave for 60 h. Complex **(17)** was obtained by through the dehydration **(16)** by heating it in a tubular furnace in a nitrogen atmosphere at high temperature (190 °C). The complexes decompose in two stages with a double weight loss, the first occurring at approx. 150-170 °C and corresponding to water molecules loss. Above these temperatures **(15)** and **(16)** decompose at 314 and 231 °C, respectively. The calculated detonation parameters show that the compounds are strong explosives, their velocity of detonation is estimated to be in the range of 8.7-8.9 km/s, with the detonation pressure being at 39.6-47.6 GPa and the heat of explosion being 1.196-1.507 kcal/g. Compound $[Pb(BTA)(H_2O)]_n$ has higher detonation parameters, decomposition temperature and crystal density than **(16)**. Compounds **(15)** and **(16)**, due to high density, thermal stability, low sensitivity and high parameters, may be used as propellant burning rate modifiers.

Table 6. Properties of BTA complexes [22, 39, 65]

Complex	**12**	**14**	**15**	**16**	**17**
Velocity of detonation (calculated) [m/s]	–	–	8923	8751	–
Theoretical pressure of detonation (calculated) [GPa]	–	–	47.66	39.61	–
Impact sensitivity [J]	>40	>40	>40	>40	33
Friction sensitivity [N]	>360	>360	–	–	–
Density [g/cm^3]	–	–	3.412	2.415	–
Temperature of decomposition [°C]	295	275	314	231	231
Nitrogen content [%]	62.0	64.0	33.50	36.07	44.01

Other interesting examples are complexes of Cu and Ni with BTA and nitramine (NH_2NO_2) with the general formula $M(BTA)(NH_3)(NH_2NO_2)$ and $M(BTA)(NH_3)(NH_2NO_2)_2$ (Figure 14) [59]. All compounds are characterized by high crystal density (over 2.0 g/cm^3) and high detonation parameters. Theoretical

values of the detonation velocity are in the range of 7.7-8.5 km/s with detonation pressures in the range of 29-36 GPa.



18 **19** **20** **21**

Figure 14. Structure of BTA and nitramine complexes

Table 7. Properties of BTA and nitramine complexes

Complex	**18**	**19**	**20**	**21**
Teoretical velocity of detonation [m/s]	7760	8480	7730	8360
Teoretical pressure of detonation [GPa]	30.08	36.12	29.47	33.80
Impact sensitivity H_{50} [J]	10.5	10.5	10.5	7.0
Density [g/cm^3]	2.23	2.25	2.18	2.10

5,5'-Azobis(1*H*-tetrazole) (AZT) consists of two 1*H*-tetrazole rings connected by an azo bridge [61]. There are only two carbon atoms and two hydrogen atoms in the compound. The compound can form ionic derivatives due to the presence of two weakly bound protons in the rings at the nitrogen atom in position 1. Compounds in the form of AZT salts have been extensively studied, in contrast to coordination compounds [61-64]. Unfortunately there is a lack in the literature of information about the coordination compound of AZT. In complex compounds 5,5′-azobis(1*H*-tetrazole) it appears as anion [64]. Compounds $[Cu(NH_3)_4](AZT)2H_2O$ and $[Cd(NH_3)_2(H_2O)_2](AZT)$ are characterized by very low impact sensitivity, lower than the copper and cadmium salts of AZT, which is the result of stabilization of the molecule by ligands. Their decomposition temperature is quite high, however, the copper complex slightly decomposes above 75 °C which is associated with the loss of water molecules, the cobalt complex showing no changes below 100 °C. The addition to the structure of copper and cobalt salts of AZT molecules of ammonia and water contributed to the stabilization of these compounds and to a decreased sensitivity to mechanical stimuli.

2.4 Coordination explosives with 1*H*-pentazole (HN_5)

HN_5 is an aromatic inorganic chemical compound with the highest nitrogen content (98.58%) among all heterocyclic compounds [65-70]. It is made up of five nitrogen atoms and only one hydrogen. A stable proton enables the formation of salts, and free electron pairs on nitrogen atoms of coordination compounds. The first compound obtained containing pentazole was phenylpentazole, with the most stable compound obtained so far being 4-dimethylaminophenylpentazole. Sun *et al.* [67] obtained a silver pentazole complex $[Ag(NH_3)_2]^+[Ag_3(N_5)_4]^-$ forming a three-dimensional skeleton without carbon atoms and water molecules. The compound is made of silver cation, ammonia molecules as ligands and pentazole anions. The isolated material is in the form of a white powder and is a stable substance. It is stable up to 90 °C at which point it begins a two-stage decomposition into metallic silver. Compared to the very sensitive AgN_5 and AgN_3 the complex is not very sensitive to impact and friction (H_{50} = 73.8 cm). The calculated crystal density, based on X-ray data, is 3.2 g/cm^3 and this is the highest density among the pentazole derivatives. The complex was obtained as a result of a multi-stage synthesisThe fFirst step was to obtain a substance of formula $(N_5)_6(H_2O)_3(NH_4)_4Cl$ containing a pentazole anion (N_5^-), which was stabilized by water molecules, ammonium cations and a chloride ion. $[Mg(H_2O)_6]^{2+}[(N_5)_2(H_2O)_4]^{2-}$ is formed as a result of the reaction between a solution of $Mg(NO_3)_2$ with pentazole complex in methanol-water solution. The obtained complex was treated with silver nitrate and ammonia, the result of which was $[Ag(NH_3)_2]^+[Ag_3(N_5)_4]^-$ with 80% yield. Obtaining the pentazole anion (N_5^-) is a breakthrough in the chemistry of high-nitrogen explosives due to the potential applications in high-density materials (HEDM), as well as a compound for the synthesis of ferrocene analogues. The authors tried to separate AgN_5 but the compound had low stability, is very sensitive to light and decomposes to AgN_3. The 1*H*-pentazole anion is stable in the form of $(N_5)_6(H_2O)_3(NH_4)_4Cl$ and $Co(N_5)_2(H_2O)_4 \cdot 4H_2O_2$ which gives wide possibilities in the synthesis of high-energy explosives.

3 Conclusions

- Among the complex compounds containing in their structure high-nitrogen ligands built of a five-membered heterocyclic ring, two groups should be distinguished: 1,2,4-triazole derivatives and 1*H*-tetrazole.
- In 1,2,4-triazole complexes the most common are 4-amino-1,2,4-triazole derivatives. Compounds with this ligand are a promising group of explosives

due to the possibility of creating various structures and thus modifying their physico-chemical properties. Due to three nitrogen atoms with an electron pair it is also possible to create multi-core compounds in which the ligand molecule connects coordination atoms. These materials are characterized by low sensitivity compared to typical primaries and good thermal stability. These compounds can be used in electric igniters and some, *e.g.* $[Cu(4\text{-}AT)_4(ClO_4)(H_2O)](ClO_4)$ are proposed as additives to pyrotechnic compositions, propellants with ammonium perchlorate.

- An interesting group are also the 3-amino-5-hydrazine-1,2,4-triazole complexes with the perchlorate anion. In addition to high detonation parameters, sensitivity to laser radiation, they have good thermal stability and decompose above 230 °C. These materials are primaries which are sensitive to laser radiation even in phlegmatized form. The distinguishing material among them is bis(4-amino-3-hydrazine-1,2,4-triazole)copper(II) diperchlorate. The material is very sensitive to mechanical stimuli, however in phlegmatized form its sensitivity is reduced to PETN or CL-20 levels. The complex has a short transition to detonation time, with the minimum amount required to initiate an RDX charge in a No. 8 igniter tube being 0.025-0.030 g. This compound does not contain heavy metals and is sensitive to laser radiation, even in phlegmatized form, so it can be a replacement for typical primaries.
- Derivatives of 1*H*-tetrazole are characterized by high enthalpies of formation, detonation parameters, and high heat of explosion values. The main component of the decomposition products of these materials is nitrogen gas, which is advantageous from an ecological point of view. Of the 1*H*-tetrazole complexes obtained, several groups should be distinguished.
- 5-Nitro-1*H*-tetrazole is the most commonly used ligand. The most popular and definitely the best coordination compound with the NT ligand is BNCP. Due to high detonation parameters, it is considered not only a primary explosive, but also a a secondary explosive in initiation systems. To stimulate the RDX, only 0.05 g of BNCP is needed. Because of high parameters, sensitivity, thermal stability and safety of work, it exceeds currently used primary explosives. BNCP is proposed as a replacement for LA and other toxic compounds in electric igniters.
- Of the other 5-nitro-1*H*-tetrazole complexes, NKT deserves attention. This material has high thermal resistance, which means it can be used for high temperature work. Also, noteworthy are NT complexes known as “green NT explosives”. These materials do not contain toxic metals or chlorate anions in the structure. They only consist of iron (II) cation, 5-nitro-1*H*-tetrazole

and water as ligands. They are stable up to 250 °C, insensitive to electric spark, and in moist form insensitive to impact, friction and flame.

- CP is another potential replacement for currently used primary explosives. In loose form it has a sensitivity at the level of secondary explosives, but when pressed is as sensitive as primaries. CP has been used in safe low voltage electric igniters. Compared to commonly used primaries it has less sensitivity to mechanical stimuli (5 J) and is safer to use.
- BTA derivatives are one of the most interesting coordination explosives. $Cu(BTA)(NH_3)_2$ and $[(NH_4)_2Cu(BTA)_2 \cdot 2.5H_2O]$ are not very sensitive to mechanical stimuli and have high thermal stability. Complexes $[Pb(BTA)(H_2O)]_n$, $[PbCu(BTA)_2(H_2O)_5] \cdot 2H_2O$ and $PbCu(BTA)_2$ are insensitive to impact, however their thermal stability is lower than those of copper analogues. The theoretical detonation parameters are high with an estimated velocity of detonation of 8.7-8.9 km/s and a pressure of detonation of 39.6-47.6 GPa.
- Also, complexes with BTA and nitroamine are characterized by high parameters and low sensitivity. Compounds containing the BTA anion in their structure have high thermal stability, low sensitivity to mechanical stimuli and very high detonation parameters. These materials are proposed as components of pyrotechnic compositions and gas generators and propellant burning rate modifiers.
- Discovery of pentazole anion (N_5^-) is a breakthrough in the chemistry of high nitrogen explosive compounds due to the synthesis of new compounds and the possibilities of their application. The N_5^- anion and its salts are unstable materials, only the form of complex with coordinated molecules of ammonia, water and ammonium cations, is stable. The obtained silver complex $[Ag(NH_3)_2]^+[Ag_3(N_5)_4]^-$ is a stable substancean is not very sensitive to impact and friction. Synthesis of this compound gives wide possibilities in the synthesis of high nitrogen explosives.
- The complexes decompose into gaseous explosion products, the main component of which is nitrogen, and into molecular metal, making the explosion products environmentally friendly and less toxic.
- In comparison to classic primaries, the complexes are characterized by greater safety of production and use. They are already successfully used in safe electric detonators.
- Complexes have lower toxicity and sensitivity to mechanical stimuli and resistance to external factors. It is estimated that they will find application not only in explosion initiation systems but also in, for example, gas generator mixtures.

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