SILESIAN UNIVERSITY OF TECHNOLOGY
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DEPARTMENT OF PHYSICAL CHEMISTRY AND TECHNOLOGY OF POLYMERS

Klaudia Pawlus, M. Eng.
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"Synteza i badanie właściwości wysokoenergetycznych związków koordynacyjnych"

"Synthesis and investigation of the properties of energetic coordination compounds"

Supervisor: Mieczysław Łapkowski, prof.

Assistant supervisor: Tomasz Jarosz, D.Sc., Ph. D., M. Eng.

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CONTENTS

List of abbreviations

1-AT - 1-amino-5H-tetrazole
1-ATRI - 1-amino-1,2,3-triazole
1-ETZ - 1-ethyl-5H-tetrazole
2-AT - 2-amino-5H-tetrazole
4-ATZ – 4-amino-1,2,3-triazole
4-IMCA - 1H-imidazole-4-carbohydrazide
5-DTP - 2,2-bis(5-tetrazolyl)propane
Ac – acetate
ADN - ammonium dinitramide
ADNP - 4-amino-3,5-dinitropyrazole
AET - 1-azidoethyl-5H-tetrazole
AG – aminoguanidine
AGHS - aminoguanidine hemesulfate
ANFO - ammonium nitrate(V) fuel oil
ANQ - 3-amino-1-nitroguanidine
ANQ·DNS - 1-amino-2-nitroguanidine-3,5-dinitrosalicylic salt
AOCA - 4-amino-1,2,5-oxadiazole-3-carbohydrazide
AP - ammonium perchlorate
ATR-IR - Attenuated total reflectance infrared spectroscopy
ATRP - atom transfer radical polymerization
atz – 5-aminotetrazole
BEMN - bis(ethylenediamine)metal(II) nitrate
BNCP - bis-(5-nitro-2H-tetrazolato-N^2)tetraammine cobalt(III) perchlorate
BNCP - di(5-nitrotetrazolium-N^2)- teraaminacobalt(III) chlorate(VII)
BNNP - bis-(5-nitro-2H-tetrazolato-N^2)tetraammine nickel(III) perchlorate
bpdc - 2,2'-bipyridine-4,4'-dicarboxylic acid
CDPA - 1-(chloromethyl)-3,5-dinitro-1H-pyrazole-4-amine
CE – counter electrode
CHZ – carbohydrazide
CN - coordination number
CoHN - trihydrazinecobalt(III) nitrate(V)
CV – Cyclic voltammetry
DAAF - 3,3'-diamino-4,4'-bifurazane

DAAT - diaminoazobis tetrazine

DAAzF - 3,3'-diamino-4,4'-azofurazane

dab – 1,4-diaminobutane

dahn - 1,7-diaminoheptane

dahx - 1,6-diaminohexane

dap - 1,3-diaminopropane

dapn - 1,5-diaminopentane

DATr - 3,4-diamino-1,2,4-triazole

DN – dinitramide

DNNG - 1-(2,4-dinitroanilino)-2-nitroguanidine

DP - 1,3-diaminopropane

DSC - Differential scanning calorimetry

DTA - Differential thermal analysis

E_{BW} - bubble gas energy equivalent

ECCs - energetic coordination compounds

EDA - 1,2-ethylenediamine

EDN – ethylenedinitramine

EN – 1,2-diaminoethane

E_{SW} - shock wave energy equivalence

Fc – ferrocene

FDCA - furan-2,5-dicarbohydrazid

FGAN - fertilizer grade ammonium nitrate(V)

fpo - 2-(furan-2-yl)-5-(pyridin-2-yl)-1,3,4-oxadiazole

H_2DNABF - 3,3'-dinitramino-4,4'-bifurazan

H_2TNPG - 2,4,6-trinitro-3,5-dihydroxyphenolate

H_2TNPG - 2,4,6-trinitro-3,5-dihydroxyphenolates

HE – high explosives

Hntz - 3-nitro-1H-1,2,4-triazole

HOSA - hydroxylamine-O-sulfonic acid

HOSA - hydroxylamino sulfonic acid

HTNR - 2,4,6-trinitro-3-hydroxyphenolate

HTPB - hydroxyl-terminated polybutadiene

IET - ignition/explosion temperature

Itp – isophthalate

LA - lead(II) azide
LS - lead(II) styphnate
MCZ - methyl carbazate
MNCuP - mono-(5-nitro-H-tetrazolato-N)triammine copper(II) perchlorate
MNZnP - mono-(5-nitro-H-tetrazolato-N)triammine zinc(II) perchlorate
MOFs – metal-organic frameworks
MTZ - 1-methyl-5H-tetrazol
mtz - 5-methyltetrazole
NHZ – nickel(II) hydrazine nitrate
NPTA - 5-(4-nitro-1H-pyrazol-3-yl)-1H-1,2,4-triazol-3-amine
NPTN - (Z)-N-(5-(4-nitro-1H-pyrazol-3-yl)-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)nitramide
PETN - pentaerythritol tetranitrate
ppot - 5-(2-phenyl-4-pyridyl)-1,3,4-oxadiazole-2-thione
PR – picrate
PRCA – 1H-pyrrole-2-carbohydrazide
pto - 2-(pyridin-2-yl)-5-(thiophen-2-yl)-1,3,4-oxadiazole
PXRD - powder X-ray diffraction
PZCA - 1H-pyrazole-4-carbohydrazide
RDX - cyclotrimethylenetrinitramine
RE – reference electrode
SCZ – semicarbazide
SEM – Scanning Electron Microscopy
TACN - tetraamine copper(II) nitrate
TAEA - tris(2-aminoethyl)amine
TAG – triaminoguanidine
TANPDO, 2,4,6-triamino-5-nitropyrimidine-1,3-dioxide
TAPA - tris(3-aminopropyl)amine
TGA – Thermal Gravimetric Analysis
TNBI - 4,4’,5,5’-tetranitro-2,2’-bi-1H-imidazole
TNNG - 1-(2,4,6-trinitroanilino)-2-nitroguanidine
TNR - 2,4,6-trinitro-3,5-dihydroxystyphnate
TNT - 2,4,6-trinitrotoluene
TZCA - 1H-tetrazole-5-carbohydrazide
WE – working electrode

1. INTRODUCTION

With the increasing demand for find new energetic materials, there is currently a growing need for finding compounds which will be characterised by lower toxicity for environment compared to those containing heavy metals such as lead, cadmium, mercury or antimony [1]. Examples of such compounds being primary explosives are lead(II) azide (LA) and lead(II) styphnate (LS), which are currently used in detonators or they are used for military purposes [2]. The following table summarizes the main energetic parameters for lead(II) azide and lead(II) styphnate.

Table 1: Detonation parameters of lead(II) azide and lead(II) styphnate [3–6].

Property	**Lead(II) azide**	**Lead(II) styphnate**
ρ **[g/cm^3]**[a]	4.80	3.00
T$_{dec.}$ [°C][b]	315	282
D [m/s][c]	5500	5200
IS [J][d]	0.089	0.025
FS [N][e]	< 1	< 1
ESD [mJ][f]	5.0	0.2
-ΔU^o [kj/kg][g]	1569	-
T$_{det.}$ [K][h]	3401	-
V$_0$ [L/kg][i]	252	-
d$_{cr.}$ [mm][j]	0.01 - 0.1	-

[a] Density
[b] Thermal decomposition temperature
[c] Detonation velocity
[d] Impact sensitivity according to the BAM drop hammer test
[e] Friction sensitivity according to the BAM friction tester
[f] Electrostatic discharge sensitivity
[g] Heat of detonation
[h] Temperature of detonation
[i] Volume od detonation gasses
[j] Critical diameter

Although LA is characterised by high detonation performance it has many disadvantages. It is hydrolytically unstable, exhibits high sensitivity to mechanical stimuli (impact, friction), and is incompatible with metals and their alloys [7]. Additionally, this compound is harmful to the human body. For instance, contact with lead through inhalation or ingestion adversely affects, among other effects, the blood, the central nervous system, leading directly to mental impairment [8]. Furthermore, a commonly used material in detonators, as well as in boosters, detonating cords is pentaerythritol tetranitrate (PETN), which belongs to the group of nitroester compounds [9]. This compound has been used since the 1930s and there are still accidents associated with its use, hence the search for replacements for this compound [10]. PETN is obtained by the esterification reaction of pentaerythritol with fuming nitric acid. PETN exhibits a friction sensitivity of 60 N and an impact sensitivity of 3-4 J [11]. Potential replacements for LA or PETN should be insensitive to moisture, light and should exhibit easy initiation capability, simultaneously being safe to handle. In addition, they should exhibit good thermal stability (exothermic decomposition above 200 °C) and also be chemically stable [12]. Finding alternative compounds for LA and PETN is a challenging issue, since such compounds should possess good high safety parameters (impact, friction), high shock wave parameters and extremely rapid deflagration to detonation transition.

Compounds that can potentially fulfill these requirements are energetic coordination compounds (ECCs) [13]. They are composed of a central atom, which is a metal cation, oxidising anion and ligand. Due to generation by them during decomposition process non-toxic gaseous products (such as carbon dioxide and nitrogen), they are often referred to as "green" explosives [14, 15]. Equally important is the possibility of simple synthesis, which does not require many stages. This is particularly important in the context of industrial-scale production. It seems beneficial to intensify research on energetic coordination compounds, whose ligands will be typical and widely used raw materials of the chemical industry or chemical compounds that can be obtained from such raw materials by simple transformations. In designing new explosives, the selection of metal ions and ligands is important, as the formation of covalent bonds and hydrogen interactions, which provides opportunities to determine the structure of the molecule. As a result of thermal decomposition of the compound molecule, these bonds, along with coordination bonds are broken, resulting in the release of a large amount of energy [16,17].

Since ECCs may exhibit properties that are intermediate between initiating and secondary explosives, they are often investigated for their use in detonators and potentially to replace to replace LA or PETN [18, 19].

2. AIM AND SCOPE OF THE WORK

The aim of the work was to identify the possibility of obtaining new energetic coordination compounds (ECCs) containing ligand in the form of aliphatic amine and to investigate them in terms of safety parameters and the possibility of practical application as "green" alternatives to replace PETN used in detonators. Accordingly, the new ECCs should maintain energetic parameters comparable to the properties of energetic materials used in the detonators such as LA and PETN. Furthermore, an important aspect of work was to obtain compounds that do not require multi-step synthesis and complex purification procedures.

The scope of the work includes the synthesis of a series of energetic coordination compounds of transition metals (Fe, Ni, Cu, Zn) containing ligands in the form of aliphatic amines (1,2-ethylenediamine; 1,3-propylenediamine; tris-(2-aminoethyl)amine and tris-(3-aminopropyl)amine) with nitrate and perchlorate anion. Ligands were selected on the basis of literature reports indicating the use of ligands in the form of aliphatic amines such as 1,2-ethylenediamine and 1,3-diaminopropane for the synthesis of ECCs. Based on that, it was decided to determine the effect of chain length and degree of branching and the associated nitrogen content of the molecule on the explosive performance. The selected anions are explosophore groups and exhibit a strongly oxidising character. The choice of transition metals was determined by the possession by these metals of unfilled valence shells and, therefore, the ability to form coordination bonds with free electron pairs on nitrogen atoms in the ligand molecule.

3. LITERATURE REVIEW

3.1. COORDINATION COMPOUNDS

Coordination compounds, also referred to as complexes are composed of ions, in which an atom (or ion), referred to the central atom, is linked by at least one coordination bond to ligands. The general formula of coordination compounds can be presented as follow:

$$[\mathrm{M(L)_n}]^{\mathrm{z}}$$

where:

M - atom or central ion

L - ligand

n - coordination number of the central ion

z - charge of the complex ion

The central atom is usually a cation or transition metal atom from the d-block of periodic table, while the ligand is the electron pair donor. The bond between the metal and ligand in a molecule is an acceptor-donor coordination bond. According to Lewis theory, the donor of the electron pair is the base, while the acceptor is the acid. Coordination compounds possess an inner coordination sphere, which is represented by a ligand, while the outer coordination sphere is represented by a counter-ion.

Considering the selection of metals forming complex compounds, literature indicates the use of transition metals of the d block elements of the periodic table, due to their formation of small ions having a large charge. These metals posses incompletely filled subshell and they are able to form a coordination bond with ligands, because of their ability co accept free electron pairs [20]. A coordination compound can have either one type of ligands (homoleptic ligands) in its structure or more than one type of ligands (heteroleptic ligands). For a chemical individual to be a possible ligand it must have at least one free electron pair. Accordingly, ligands can be either anionic, containing an atom of an element from groups 14-17 of the periodic table - such as Cl^-, Br^-, I^-, OH^-, CN^-, or neutral - H_2O, NH_3, CO, NO, or amines.

A term that is related to coordination compounds is the coordination number (CN). This is the number of number of atoms, molecules or ions bonded directly to the central ion (the number of attached ligands). CN usually takes the values of pair numbers in the range of 2 - 8 and indicates the spatial structure of the distribution of donor atoms around the central atom, corresponding to a specific geometry for example octahedral, tetrahedral, and square planar. The coordination number depends primarily on the charge of the ligand, polarizability and acceptor properties of cations, the nature of the coordination bond and the state of aggregation of the complex.

3.2. ENERGETIC COORDINATION COMPOUNDS

For ECCs, the metal selection for the synthesis is important issue. The literature indicates the use of transition metals such as nickel, copper, iron, zinc and cobalt [21, 22]. This is determined by the possession of an unfilled subshell by these metals, so that they exhibit the ability to accept electron pairs and form coordination bonds. In addition, the work on new ECCs assumes that compounds of this type will not contain toxic metals as in the case of lead-containing compounds such as lead(II) azide.

Energetic coordination compounds may contain ligands, such as hydrazine [23], ethylenediamine [24], carbohydrazide [25]. There are also ligands containing aromatic rings, including heterocyclics like 1-aminotriazole, 3,4-diaminotriazole, 1-aminotetrazole [26, 27]. Ligands in ECCs should posses a higher content of nitrogen atoms in a molecule, in comparison to a high content of carbon atoms [28]. The selection of individual components of the structure of ECCs makes it possible to influence their physicochemical and energetic properties. The stability of such compounds depends on the strength of the coordination bonds, which in turn depends on the type of ligand used and also the metal constituting the coordination center.

The anions, which are incorporated into ECCs, can serve as an oxidiser by improving the oxygen balance and heat of explosion. In turn, incorporation explosophore groups into molecule, such as NO_3^-, ClO_4^- allows the introduction into the molecule additional nitrogen or oxygen atom, improving the energetic properties of the molecule [29]. These parameters, in turn, are related to the parameters of the detonation process, affecting, for example, the increase in detonation velocity [30]. Oxidising anions can also be found in the form of ions: ClO_3^-, NO_2^-, IO_3^-, IO_4^-, BrO_3^- and MnO_4^- [31]. These anions serve as a complementary ion for the cations of the complex and enable the release of large amounts of active oxygen. In the literature, it is common to find Cu-containing coordination compounds derived from $Cu(ClO_4)_2$ salts, due to the possibility of strong coordination ability and formation of stable coordination compounds. Coordination compounds containing oxidising anion ClO_4^- possess higher detonation performance [32, 33].

Although the literature indicates many examples of ECCs, their energetic parameters (e.g., pressure and detonation velocity) are often simulated parameters, calculated on the basis of various programs (e.g., EXPLO5). Therefore, in many cases, there is a problem of reliably investigating their properties, which consequently affects their potential application. Examples include compounds containing the ligand in the form of ethylenedinitramine [34], or those containing oxadiazoles [35], or 1,2,4-triazoles [36, 37] which are described further in the work.

3.2.1 Synthesis of energetic coordination compounds

Literature indicates that there are various routes for synthesising energetic coordination compounds such as hydrothermal/solvothermal method [38], solid state reactions of metal hydroxide or carbonate salts [39] or direct electrosynthesis [40], but the most commonly used method is a direct preparation from metal salts and ligands in solution, e.g. in a one pot regime [38]. Typically, water is used as a reaction medium in this procedure, both due to the high solubility of raw materials, as well as synthesis products and the low environmental impact of water. In addition, metal salts are typically available as hydrates, e.g. $Fe(NO_3)_3 \cdot 9\,H_2O$ or $Cu(NO_3)_2 \cdot 3\,H_2O$, rather than in the form of anhydrous compounds. This is due to the fact that manufacture of most metal salts involves their isolation from aqueous solutions [41].

In a case where the ligand is insoluble in water, various organic solvents such as acetone, acetonitrile, dimethylformamide, dimethylsulfoxide, ethers or alcohols (e.g., methanol, ethanol) may be used [42]. After obtaining a coordination compound, the compound must be isolated from solution, e.g. through: [41]:

- crystallization of product from cooled solution by using an ice bath - as a result of lowering the temperature, the solubility is reduced thus facilitating crystallization;
- concentration of a solution using a rotary evaporator;
- adding to the reaction mixture a non-aqueous solvent, e.g. ethanol in which the product is only weakly soluble, until the product begins to precipitate from the reaction mixture;
- introduction of an excess of another anion salt (such as Na^+ or K^+) into the reaction mixture, resulting in a salt with a higher concentration of another anion and lower solubility, which is able to crystallize;
- evaporation of the resulting product to dryness and recrystallization from a non-aqueous solvent in which the product is difficult to dissolve; sublimation or distillation of the resulting product after removal of the solvent

Obtained by direct synthesis of ECCs from a solution of a metal salt and a ligand, they are often not well purified, as the precipitation of the product from the solvent at room temperature leads to the attachment of a water molecule to the ligand. As the water undergoes strong coordination to the ligand, its subsequent removal is problematic. On the other hand, the water content of the compound influences, for example, the sensitivity parameters (reducing sensitivity for friction and impact) as for example for PETN, however, it can reduce the detonation parameters [10], or as in the case of ANFO (ammonium nitrate-fuel oil) [43]. Most of the syntheses of ECCs described in the literature only indicate purification of the compounds using, for instance, ethanol, which does not always lead to proper purification, still affecting the presence of coordinated water in the molecule.

Moreover the problem of presence water in energetic compounds may be associated with the diminishing the energetic properties which may also affect on the breakdown of the crystal structure (decrease in crystal density). Crystal water tends to attach by metal in the case of ECCs to the ligand through hydrogen bonding [44]. However, hydrates of compounds are not preferable and should be avoided, while if they are formed, the water of hydration should be removed [45].

3.2.2 Energetic coordination compounds containing ammonia ligands

According to literature reports, the simplest energetic coordination compounds are those containing ammonia. Ammonia has a free electron pair on the nitrogen atom, which forms a coordination bond with the metal cation [46]. The most common example of a energetic coordination compound containing ammonia as a ligand is tetraamine copper(II) nitrate (TACN). TACN is characterised by high sensitivity to mechanical stimuli (impact sensitivity is 4 J) and also a small critical diameter (< 4 mm). With a density of 0.87 g/cm^3, the compound detonates at a velocity of 3500 m/s. The authors of the work [47].

Another example of compounds containing ammonia as a ligand are hexaammine perchlorates of transition metals (Cu, Co, Ni, Zn) is $[Cu(NH_3)_6](ClO_4)_2$. These compounds are used as burning rate modifiers in solid rocket fuels due to the simultaneous presence of a reducing (NH_3) and an oxidising (ClO_4) group in the molecule [48].

The literature also reports on compounds, such as $[Co(NH_3)_4(NO_3)]NO_3 \cdot 0.5\,H_2O$ [49], which exhibits sp^3 hybridization, characteristic for the cobalt atom in coordination compounds. The outer coordination zone consists of a NO_3^- ion and H_2O, which is connected to the inner coordination zone through hydrogen bonds (the presence of crystal water in the structure of the complex).

3.2.3 Energetic coordination compounds containing hydrazine ligands

Hydrazine (Hz - N_2H_4), due to its 87.42 wt. % content nitrogen, is frequently used as a ligand in the synthesis of energetic coordination compounds. Due to the presence of free electron pairs on both its nitrogen atoms, Hz can form bidentate coordination compounds. Hydrazine can form four types of bonds with a metal, i.e. one-cleavage model, two-cleavage model, cis-bridge and trans-bridge (Fig. 1) [50]:

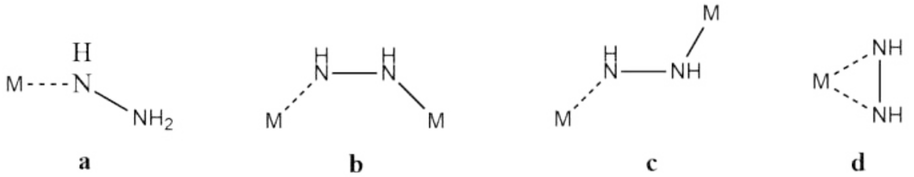


Figure 1: Scheme of hydrazine binding modes to metal.

This group of ECCs is well-exemplified by the widely studied nickel(II) hydrazine nitrate (NHN). This compound may be obtained in several ways, allowing control of the solid crystallinity of the product. The first manner is dissolving nickel powder in a solution of ammonium nitrate in hydrazine hydrate. Another way is adding alcoholic hydrazine hydrate to the aqueous solution of the metal salt [51]. A further method is based on preparing solid hydrazine mononitrate by potentiometric titration of hydrazine hydrate with nitric acid and then dissolving it in a nickel nitrate solution. However, the most straightforward method consists of slowly adding hydrazine solution at elevated temperature (about 60 °C) to an aqueous solution of nickel(II) nitrate with continuous stirring. After the completion of the reaction and cooling of the mixture, the precipitate is filtered and then dried [52]/

NHN exhibits relatively high detonation parameters, with a reported velocity of detonation of 7000 m/s and detonation pressure of 20.8 GPa for the compound at a density of 1.7 g/cm^3. It is relatively sensitive to impact and friction (10 J and 24 N respectively) and shows high sensitivity to electrostatic discharge (0.02 J). Conversely, it is relatively resistant to heating, with a decomposition temperature of 218 °C [53]. Compared to the properties of LA (Table 1), this compound is less sensitive to both mechanical stimuli and electric discharge, which is a crucial issue in the context of its use as an initiating explosive in conventional detonators.

Another example of hydrazine-containing ECCs is trihydrazinecobalt(III) nitrate(V) (CoHN) [54]. Unlike the nickel-containing compound, it exhibits lower sensitivity to impact (> 25 J), friction (60 N), as well as lower sensitivity to electrostatic discharge is 2.25 J. DSC measurements indicate that thermal decomposition of CoHN occurs at 188 °C. Due to its properties, the compound can be classified as a secondary explosive, which may find application as a additive in propellant compositions increasing the burning rate in comparison with ammonium perchlorate used in propellants. In addition to hydrazine nitrates containing Ni and Co, compounds containing Zn (ZnHN) and Cd (CdHN) can also be found in the literature [55]. Compounds with zinc, due to their high sensitivity to impact and friction, limit their potential application.

Literature also reports ECCs containing hydrazine ligands and azide anions (N_3^-), exhibiting an even higher nitrogen content than ECCs containing only hydrazine ligands. These compounds have been reported to be thermally stable and not very sensitive to mechanical stimuli. An example of such a compound is zinc(II) hydrazine azide $[Zn(N_2H_4)_2(N_3)_2]_n$ (metal azide complex), in which the zinc cation is coordinated by two azide groups and four nitrogen atoms from the bidentate hydrazine ligand [56]. These compound can be synthesised by reacting $Zn(OAc)_2 \cdot 2H_2O$ and hydrazine hydrate and sodium azide in aqueous solution at elevated temperature (70 °C). The paper also determines the results of friction and impact sensitivity testing. In the case of impact sensitivity, 50 % firing rate (h_{50}) is eqaul 28.5 cm (10 kg drop hammer) and for friction sensitivity 48 % firing rate (struck horizontally with a 1.5 kg hammer at a 90° angle).

3.3. Energetic coordination compounds containing aliphatic ligands

Energetic coordination compounds may contain simple aliphatic ligands such as 1,2-ethylenediamine (EN), ethylenedinitramine (EDN), 1,3-diaminopropane (dap), 1-4-diaminobutane (dab), aminoguanidine (AG), 3-amino-1-nitroguanidine (ANQ), triaminoguanidine (TAG), carbohydrazide (CHZ) as shown in the figure below (Fig. 2).

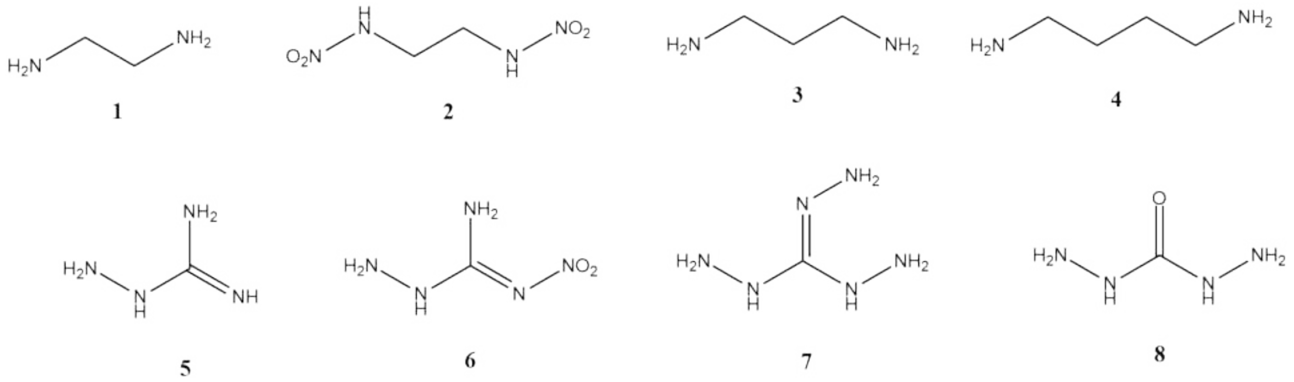


Figure 2: Examples of aliphatic ligands incorporated in energetic coordination compounds.

Ethylenediamine/ethylenedinitramine

Ethylenediamine (EN, 1,2-diaminoethane) (Fig. 2 structure 1) is an aliphatic compound containing 46.61 wt. % of nitrogen in its structure. It has two free electron pairs on the nitrogen atoms by which it can form coordination bonds with metal. This compound is frequently encountered in the literature as a ligand in energetic coordination compounds, which decompose producing gaseous products such as CO_2, N_2, H_2O [57].

The paper [58] presents examples of ECCs containing the ligand as EN, which discusses synthesis and characterization of four compounds - bis(ethylenediamine)metal(II) nitrates (BEMN) - $[M(EN)_2](NO_3)_2$, where M is the corresponding metal - Cu, Co, Ni, Zn. The synthesis of the compounds involved the preparation of ethanolic solutions of salts of the corresponding metal nitrates, into which ethylenediamine was introduced in portions with continuous stirring. In order to purify the obtained compounds, they were washed with methanol. The compounds can be ordered by increasing thermal stability and activation energy in the following order Cu < Co < Ni < Zn. Considering the compounds containing the perchlorate anion, the thermal stability of the complexes decreases in the following order: $[Zn(EN)_2](ClO_4)_2$ > $[Mn(EN)_2](ClO_4)_2$ > $[Ni(EN)_2](ClO_4)_2$ > $[Cu(EN)_2](ClO_4)_2$ > $[Co(EN)_2](ClO_4)_2$ [59]. Abovementioned compounds find application in AP (ammonium perchlorate) and HTPB (hydroxyl-terminated polybutadiene) based rocket fuels as burning rate modifiers, affecting an increase or decrease in burning rate (e.g., increased value for $[Cu(EN)_2](NO_3)_2$, the burning rate is 2.21 mm/s; decreased value for $[Zn(EN)_2](NO_3)_2$ - 1.35 mm/s) [58].

The literature indicates that EN has also been used as a ligand in compounds containing the transition metal tris(ethylenediamine) metal(II) diacetate - $[M(EN)_3](OAc)_2$ (where: M = Mn, Fe, Co, Ni, Cu and Zn). All the reported compounds contain a metal on the +2 oxidation state and are further coordinated by three bidentate ethylenediamine ligands and two uncoordinated acetate anions (Fig. 3) [60].

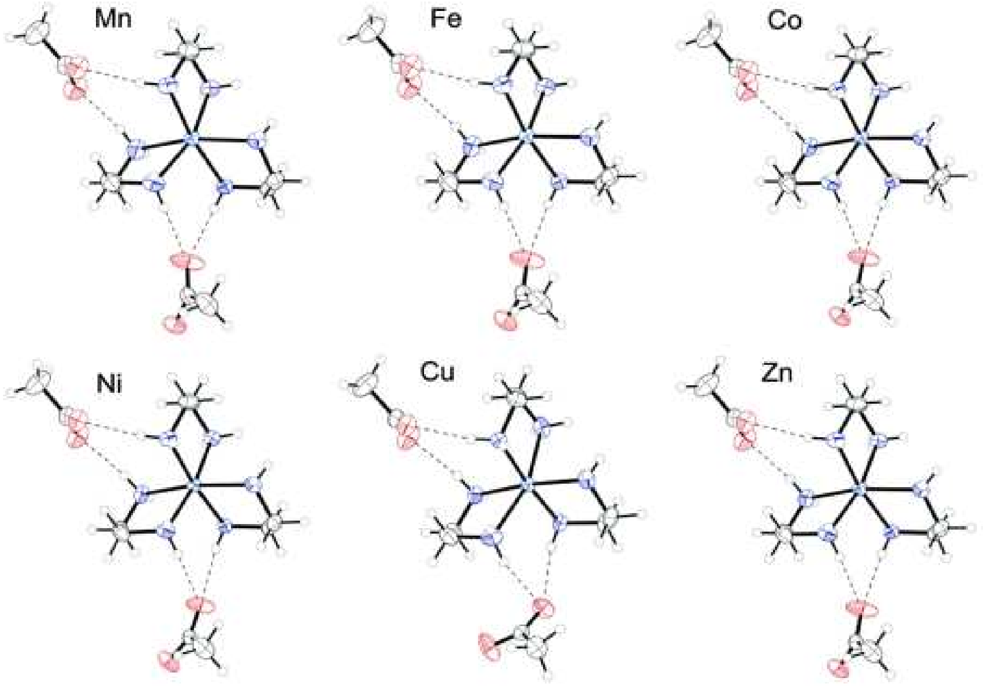


Figure 3: The isostructural asymmetric units of the $[M(EN)_3](OAc)_2$ complexes.

In this groups of compounds, the distance between a metal atom and a nitrogen atom in a molecule decreases with the order of the subsequent group of the periodic table of elements, Mn > Fe > Co > Ni > Cu > Zn [60]. ECCs containing ethylenediamine and zinc, depending on pH (0-14), can exist in different forms and therefore be more or less stable (different coordination number). An example of the forms of the compound, can be the molecular form EN, protonated HEN^+ and diprotonated H_2EN^{2+} (trans conformation). For the compound $[Zn(EN)]^{2+}$, Zn, N and C atoms arranged at the vertices of a non-planar pentagon, obtain a coordination number of 2. On the other hand, the use of an aqueous solution of zinc(II) allows to obtain a compound with a coordination number of 4 or 6, on account of the introduction of two or four water molecules into the inner sphere of the complex. For water-containing complex compounds $[ZnEN_2(OH_2)]^{2+}$ and $[ZnEN_2(OH_2)2]^{2+}$, there is no additional coordination and the existence of the compounds is possible at $pH > 10$. In addition, it is possible to exist stable compounds with Zn^{2+} in acidic environments such as $[ZnHEN]^{3+}$, $[Zn(HEN)_3]^{5+}$ [61].

Authos of the paper [62] indicate the synthesis of ECCs containing EN as a ligand with nickel nitrate and perchlorate analogue. The synthesis was carried out in several ways. One was a solvent-free synthesis using nickel nitrate hexahydrate (alternatively, perchlorate analogue). In this case, the advantage was to avoid the step of separating the compound from the solvent as well as to avoid the drying step, and most importantly to obtain coordination compounds containing no water in the structure (water-free ECCs). Consequently, the compounds $[Ni(C_2H_8N_2)_2](NO_3)_2$, $[Ni(C_2H_8N_2)_3](NO_3)_2$ and also $[Ni(C_2H_8N_2)_3](ClO_4)_2$ were obtained, for which the composition was determined taking into account the molar ratio of ethylenediamine to nickel salt. The synthesis with solvents involved mixing solutions of nickel salts and ethylenediamine containing ethanol and the resulting crystals were washed with cooled water and then with ethanol. The paper also indicates that the obtained compounds show thermal stability up to 200 °C, while above they degrade one- or two-step. The compound containing three ethylenediamine molecules and a perchlorate anion displayed the lowest stability. The contrary situation occurred in the nitrate analogue. A higher amount of ethylenediamine in the molecule resulted in a decrease in the decomposition temperature. All of the compounds obtained were used as precursors for CO_2 methanation catalysts.

Another example of a compound containing ethylenediamine is Cu-based ECCs, containing nitroform [63]. Nitroform, possesses three nitro groups on the carbon atom, while due to the strong acidity of the compound and low decomposition temperature (298 K) [64] it tends to be used with other compounds that have greater stability. The compound can occur in the form of nitroformate salts, such as hydrazine nitroformate, which is a strong oxidizer which may find applications as an alternative to ammonium perchlorate used as a component of rocket fuels [65]. Considering safety parameters, both compounds do not exhibit sensitivity to impact and friction however, they are sensitive to flame. In work [63], flame sensitivity was evaluated with height for a 50 % probability of explosion, indicating that for the Cu-containing compound, it is 34.42 cm and for the Cd-containing compound it is 15.90 cm.

A derivative of ethylenediamine is ethylenedinitramine (H_2EDN (Fig. 2 structure 2), which may be used as a ligand or anion in energetic coordination compounds [34]. There are several ways to synthesise this compound, one of them includes the use of derivatives of the diamine compound using ethylene bisurethane or by nitration of 2,3-piperazinedione monohydrate using acetic anhydride and 98 % nitric acid with subsequent ammonolysis. Another way can be direct nitration of 2-imidazolidinone using 100 % HNO_3 at 0 °C, followed by hydrolysis in water at 100 °C [66]. This compound may be used as a secondary explosive and a booster explosive [66,67]. In addition, H_2EDN exhibits a strong acidic character ($pK_{a1} = 5.31$ and $pK_{a2} = 6.64$), so in order to reduce acidity and be able to use it in energetic compounds as a building block, it undergoes cocrystallization, improving the stability of the compound [68].

There are not a large number of ECCs containing H_2EDN in the literature, however there are some information regarding using H_2EDN as a ligand. It is possible to obtain ECCs with silver(I) or copper(II). On the other hand, due to the low acidity of H_2EDN and use of sodium salt during synthesis of energetic coordination compounds with manganese(II), iron(II) or zinc(II) salts is not possible. Consequently, the reaction results in the formation of the corresponding hydroxides or ethylenediaminetramide alkali salts. It is feasible to prepare coordination compounds containing copper(II) salts by in situ reaction of H_2EDN with sodium carbonate in water, and subsequently by reaction with copper(II) sulfate pentahydrate to form CuEDN (copper(II) ethylenedinitramide) (Fig. 4) [34,66]. The synthesis of ECCs containing CuEDN involves reaction with either an aqueous solution or in an aqueous ammonia solution [69].

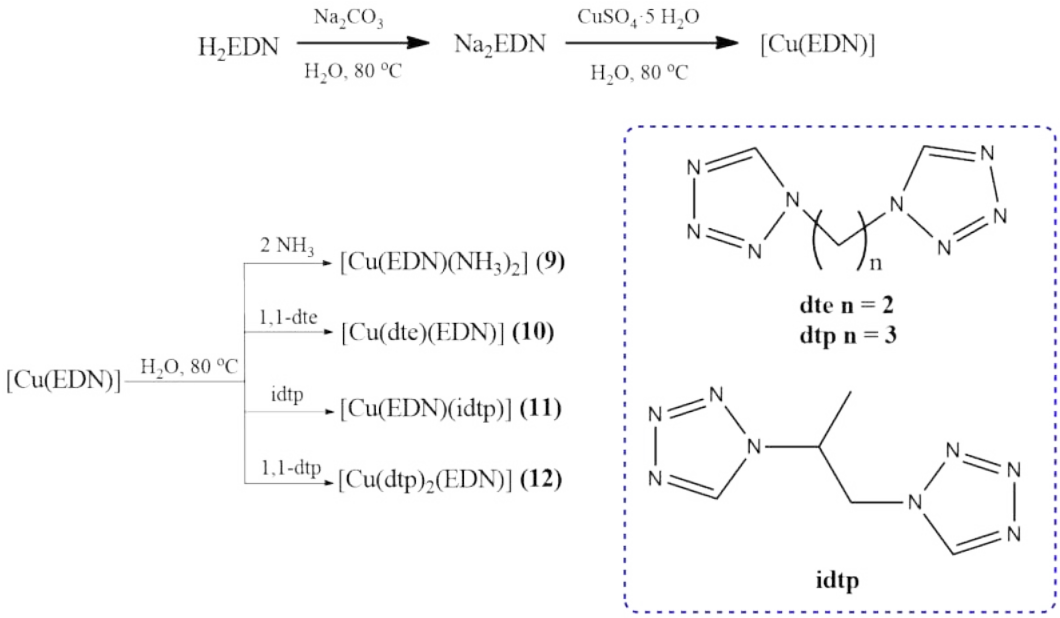


Figure 4: Scheme for in situ synthesis of CuEDN and energetic coordination compounds containing CuEDN.

The following table 2 presents the basic energetic properties of CuEDN containing compounds [34].

Table 2: Physiochemical and energetic properties of CuEDN containing energetic coordination compounds.

Compound	IS [J]	FS [N]	ESD [mJ]	HP[a]	HN[a]	T $_{dec.}$ [°C]
9	3	180	>1500	defl.	dec.	212
10	10	48	106	defl.	dec.	203
11	<1	64	106	defl.	dec.	180
12	10	60	250	defl.	dec.	177

[a] HP, HN: def. - deflagration; dec. - decomposition

1,3-diaminopropane; 1,4-diaminobutane

The use of organic aliphatic amines as ligands in the synthesis of energetic transition metal coordination compounds with a chelating function began with the use of hydrazine. The development of work on new ECCs containing aliphatic diamines, included the use of compounds with increasingly longer chains such as 1,3-diaminopropane (dap), 1,4-diaminobutane (dab), 1,5-diaminopentane (dapn), 1,6-diaminohexane (dahx) and even 1,7-diaminoheptane (dahp) [70]. Longer-chain ligands have been used less frequently due to the formation of coordination compounds exhibiting less stability. The literature indicates that it is possible to introduce substituents into the compound molecule, affecting their functionality [71], such as pyridine-2,6-dicarboxylic acid dianion, which causes blocking of sites in the coordination sphere of the metal ion [72]. The coordination compounds may be form with transition metals from the d block of the periodic table, occurring mostly as divalent metals (Mn, Fe, Co, Ni, Cu, Zn), which react with N- and O-donor ligands and their properties are similar [70]. The exception is the Co^{2+} ion, which in the presence of atmospheric oxygen causes oxidation to Co^{3+}, hence it is reasonable to conduct syntheses with cobalt salts a inert atmosphere [73]. The situation is similar for coordination compounds containing dap and Fe. Depending on the conditions for carrying out the reaction (in the air or inert atmosphere), iron occurs in the form of Fe^{2+} or Fe^{3+}. The paper [70] describes the synthesis of the above iron-containing compounds, obtaining $[Fe^{II}(Piv)_2(dap)_2]$ and $[Fe^{III}{}_4O_2(Piv)_8(dap)_2]$, respectively (where: piv - pivalate anion) and their magnetic properties and thermal behavior.

The literature also indicates the occurrence of energetic coordination compounds with 1,3-diaminopropane containing Zn [74, 75], in which the Zn atom mostly exhibits a distorted tetrahedral geometry [76], as well as a distorted geometrical trigonal bipyramidal [77]. Additionaly, Zn may by is used in catalysis on the basis of its low toxicity [78, 79]. One example of Zn-based ECCs is $[Zn(dap)(NCS)_2][Zn(dap)(NCS)_2]_n$ [80]. The structure of the compound is composed of two types of molecules - the first one is monomeric ($[Zn(dap)(NCS)_2]$, in which Zn atom binds to one terminal dap molecule and to two N-linked thiocyanate anion (NCS^-). Second type of molecule structure is polymeric $[[\mathrm{Zn(dap)(NCS)_2}]_2]$ in which dap act as bridging ligand. The following figure shows the monomeric structure (Fig. 5).

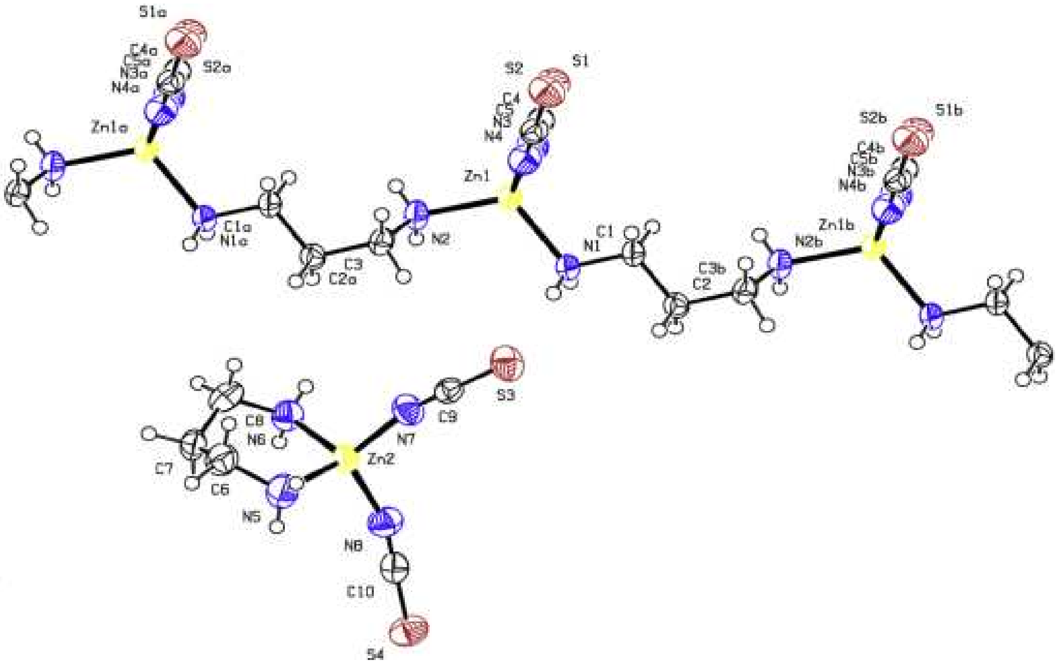


Figure 5: Structure of $[\mathrm{Zn(dap)(NCS)_2}][\mathrm{Zn(dap)(NCS)_2}]_3$ coordination compound [80].

This figure illustrates that the zinc atom adopts a distorted tetrahedral geometry. Occurring in the molecule, 1,3-diaminopropane, is capable of forming a six-membered ring, while in the case of a polymeric molecule, it adopts a linear chain structure. The researchers indicated that a strong hydrogen bond is present in the dap molecule between the C–H and N–H atoms and the sulfur atoms of the thiocyanate, allowing the compound to remain stable [80].

In energetic coordination compounds, copper is mainly found in the second oxidation state, Cu(II), due to its ability to form compounds with diversified geometries: tetrahedral, square planar, trigonal bipyramidal, square pyramidal and octahedral [81]. Thus, copper(II) ions exhibit high coordination ability, especially with N-donor compounds (e.g., aliphatic diamines). Copper in the first oxidation state - Cu(I) is less preferable, due to its ability to form compounds with mostly tetrahedral geometries [82]. Ligand in the form of 1,3-diaminopropane used in ECCs is capable of coordinating with Cu(II) ions in a bent or planar conformation. Many syntheses using this ligand may be found in the literature, which mainly describe the conformation and geometry of the obtained compounds [83, 84]. The authors of the paper [85], in turn, attempted to obtain different isomers of the same compound $[\mathrm{Cu(dap)_2Cl_2}]$, characterised by different physical properties, which is important from the point of view of designing new materials. The possibility of obtaining different isomers of the compound, resulted from minor changes of the syntheses. The synthesis involved the preparation of a methanolic solution of $\mathrm{CuCl_2 \cdot 2H_2O}$, into which 1,3-diaminopropane was gradually introduced with continuous stirring. As a result of the reaction, a navy blue-colored precipitate, which dissolves in an excess of solvent, and a blue-colored precipitate, which is insoluble, were obtained in the reaction vessel. This precipitate was separated by gravity, while the navy blue precipitate was separated by slow evaporation of the solvent. In the next step, the navy blue precipitate was washed with diethyl ether and dried. In an attempt to obtain the third isomer, concentrated hydrochloric acid was dropped into the navy blue precipitate, yielding a yellow-colored precipitate. In the next step, this precipitate was washed with diethyl ether to elute chloride ions. As a result, three isomers of [Cu(dap)$_2$Cl$_2$] were obtained, the geometry of which is shown in the figure below (Fig. 6) [85].

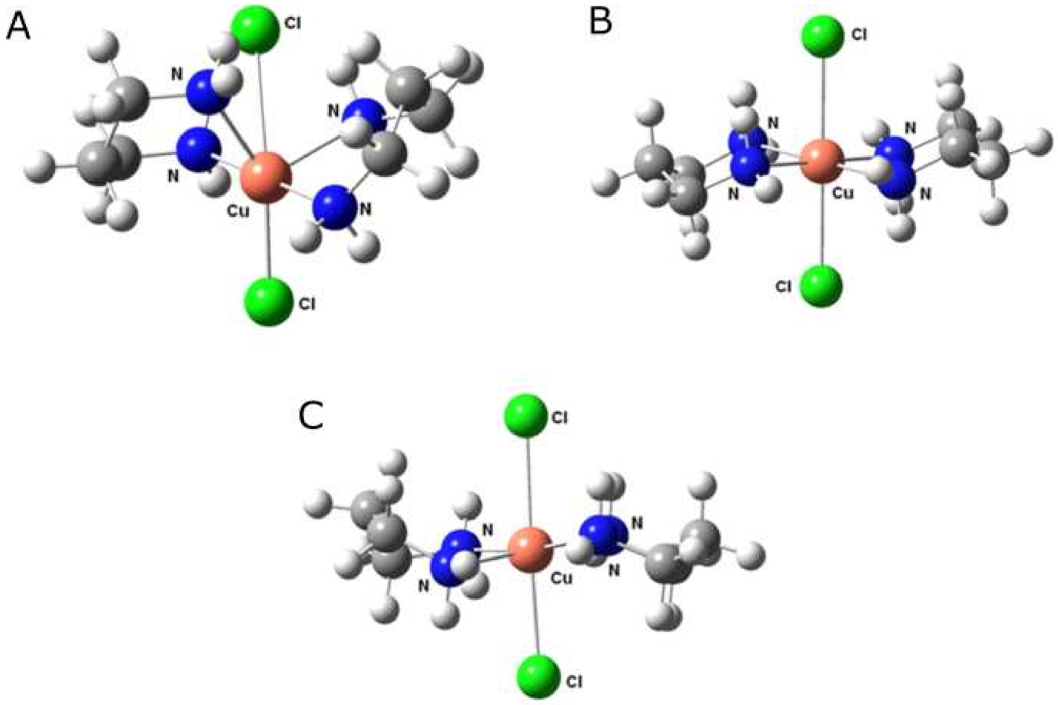


Figure 6: Different geometries for [Cu(dap)$_2$Cl$_2$]. Where A: boat–boat (navy blue); B: chair–chair (blue); C: chair–boat arrangements (yellow).

In all obtained compounds, copper is located in the center of spatial symmetry and is coordinated with 1,3-diaminopropane, forming a six-membered ring. According to density functional theory (DFT) calculations, there are differences in energy among all isomers - between isomer 1 and 3 it is 3.12 kJ/mol, between 1 and 2 and 2 and 3 it is 11.26 and 8.19 kJ/mol, respectively. It follows that isomer 2 is the most stable. The change in the color of the obtained compounds is due to non-planarity of the ligand molecule.

Another example of a compound containing Cu and dap is [Cu(ClO$_4$)(dap)$_2$(H$_2$O)]ClO$_4$ [86]. Its synthesis involved slowly dropping an ethanolic solution of dap into an aqueous solution of copper(II) hexahydrate perchlorate and then filtering the unreacted reactants. Crystals of the compound were separated from the solution. The molar ratio of copper salt to ligand used was

1:2. Based on XRD analysis for the monocrystal, it was found that the copper atom exhibits a distorted octahedral coordination sphere and is coordinated in the equatorial plane by the two nitrogen atoms present in the ligand molecule, while the O atoms are in the axial position. Obtained compounds exhibit monoclinic space crystal system.

1,3-diaminopropane can also occur as a chelating ligand in the coordination polymers $[Ni(ipt)(dap)_2]_n$ and $[Cu(ipt)(dap)H_2O]n \cdot nH_2O$ (where itp: isophthalate) forming a zig-zag structure [87]. Obtaining the compound $[Ni(ipt)(dap)_2]_n$ is possible by reacting methnolic solutions of dap and $NiCl_2 \cdot 6H_2O$, followed by the addition of H_2ipt. The difference in the synthesis of $[Cu(ipt)(dap)H_2O]_n \cdot nH_2O$ was that an aqueous solution of dpa followed by H_2ipt was introduced to a suspension of copper(II) hydroxide carbonate in water. However, this synthesis yielded only a mono-1,3-diaminopropane derivative of copper(II) isophthalate. Based on XRD investigations, both compounds were found to exhibit a crystalline orthorhombic structure. On the basis of TG analysis, the compounds were found to be thermally stable. The compound $[Ni(ipt)(dap)_2]_n$ exhibits thermal stability up to a temperature of 283 °C, while above this, one dap molecule breaks off and at 315 textsuperscript○C and decomposition occurs. On the other hand, for $[Cu(ipt)(dap)H_2O]_n \cdot nH_2O$ two-step decomposition from 180-230 °C was observed.

Another coordination compound incorporating dap is $[Cu(bpdc)(dap)(H_2O)] \cdot 2H_2O$ (where 2,2'-bipyridine-4,4'-dicarboxylic acid ($bpdcH_2$) [88]. The synthesis of the compound involved mixing a methanolic solution containing 1,3-diaminopropane with an aqueous solution of 2,2'-bipyridine-4,4'-dicarboxylic acid and then introducing the mixture into $CuCl_2 \cdot 2H_2O$ and stirring at elevated temperature (60 °C). XRD crystallographic data indicated that the resulting compound is characterised by an orthorhombic crystalline structure and there are hydrogen bonds (N−HO, O−HO and C−HO) in the structure of the compound, while the presence of intermolecular bonds provides stability to the molecule.

As mentioned previously, energetic coordination compounds containing 1,4-diaminobutane can also be found in the literature, classified as materials displaying intermediate properties between initiating and secondary explosives. This ligand exhibits a neutral bidentate character, in turn complexing with the NO_3^- anion, makes it possible to obtain compounds showing energetic properties. The presence in the structure of the compound simultaneously of a reducing and an oxidising group ensures high exothermic decomposition [89]. Singh et. al. obtained 4 ECCs containing Zn, Cu, Ni, and Mn and a NO_3^- anion [90]. The authors of the paper also indicated that the thermal stability of the obtained compounds increases in the order Mn < Cu < Ni < Zn. Thermal decomposition proceeds in multiple stages, with two decomposition stages for compounds with Zn, four stages for compounds with Ni and Cu, and three stages for compounds with Mn. The first decomposition, endothermic, is mostly associated with dehydration of water from the molecule, the next with detachment of the ligand molecule, followed by decomposition of the residue. In addition, due to their low impact sensitivity (insensitive from a drop to 110 cm at 2 kg) [91], they may find application as potential ballistic modifiers for composite solid fuels [58]. The addition of ECCs in solid rocket fuels, affects the increase in burning rate (catalyzing the combustion process), by producing reactive metal oxides, e.g. ZnO, CuO, as a result of the combustion reaction.

Overall, the literature indicates that there are energetic transition metal coordination compounds containing a ligand in the form of difunctional amines. Most authors of works, mainly focus on determining their crystal structure and basic kinetic and thermal parameters. There are few works discussing the applications of these compounds in the energetic materials industry, only in the context of their use as burning rate modifiers in solid rocket fuels.

Aminoguanidine and derivatives

Aminoguanidine (AG) (Fig. 2 stucture 5) is another example of ligand with bidentate character, employed in ECCs. Coordination compounds of transition metals with a ligand in the form of AG, or its derivatives, are a numerously studied group of compounds due to their occurrence in many industries. The compounds also, in addition to the energetic materials industry, are used in pharmacology, physiology and also have applications in catalytic and analytical areas [92, 93]. An example of ECCs containing AG is the chelate complex $[Cu(AG)_2](ClO_4)_2$, which can be obtained by the complexation reaction of copper(II) perchlorate with aminoguanidine hemesulfate (AGHS) **(13)** [94]. This compound has a five-membered CuN_4 ring and forms a slightly deformed square planar coordination. Considering the energetic properties, DSC analysis enabled the determination of the thermal decomposition temperature of 215 °C. In addition, the compound obtained by the authors of the paper [94], is characterised by a relatively high sensitivity to mechanical stimuli - sensitivity to impact is 4 J, in turn, sensitivity to friction is 20 N. The compound is also sensitive to electrostatic discharge (0.45 J). There is also coordination compound such as $[Cu(AG)_2][DN]_2$ (where: DN - dinitramide), in which, as for $[Cu(AG)_2](ClO_4)_2$, the Cu(II) atom is four-coordinated by two N atoms of imine and two N atoms of amine originating from two aminoguanidine ligands [95]. $[Cu(AG)_2][DN]_2$ can be obtained by adding to an aqueous solution of AGHS, a sodium carbonate solution and then introducing an aqueous mixture of $CuSO_4 \cdot 5H_2O$ and ammonium dinitramide (ADN), as shown in the figure below (Fig. 7).

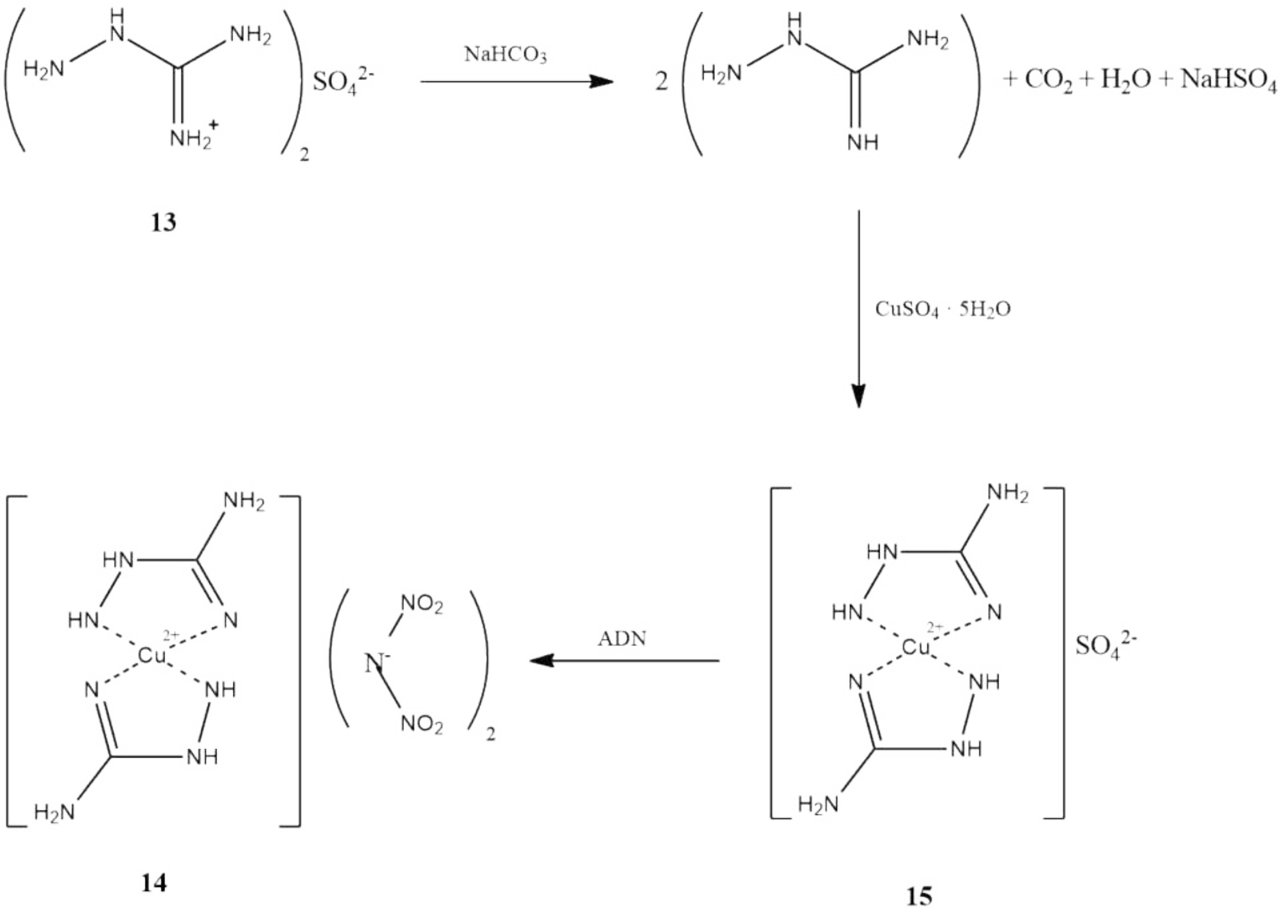


Figure 7: Synthesis scheme of $[Cu(AG)_2][DN]_2$ [95].

The authors of the paper [95] indicate that rapid thermal decomposition of the compound occurs at 130 °C. In addition, the compound in powder form is relatively sensitive to impact (3.5 J) and friction (40 N). In contrast, for a single crystal of the compound, the sensitivity to impact is less (10 J). The literature indicates that DN salts, such as a mixture of 26.2 % guanidine nitrate and 73.8 % dinitraze salt of tetramminecopper(II), are currently used in gas-forming preprates [96].

Derivative of aminoguanidine is 3-amino-1-nitroguanidine (ANQ) (Fig. 2 structure 6). One of the many advantages of using ANQ is its high electron density at the amine and nitramine substituents or lower sensitivity to impact, friction and electrostatic discharge. The compound is stable in air, despite the circumstance that other guanidine derivatives that have amine substituents undergo oxidative decomposition. The synthesis of ANQ, which is a guanidine derivative containing both an amine group and a nitro group, is possible by hydrazinolysis of nitroguanidine. In addition, ECCs with AG-derived ligand represent an attractive field of research because of their special activities in pharmacology, physiology and a broad spectrum of applications in clinical, analytical and catalytic areas [94, 97]. Aminoguanidine has found application, for example, as a usable compound in cyclization reactions allowing to obtain bis-nitraminotriazoles or in the synthesis of 5-nitriminotetrazole. ANQ is also used as a ligand in the synthesis of nitrate and perchlorate energetic coordination compounds containing metals such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ag^{+} [98]. In the same paper we can also find information about synthesis of ANQ complexes containing dinitramide counter ion for cobalt and nickel complexes **(compound 22 and 23** (Fig. 8) [98] by the addition of ammonium dinitramide to the corresponding metal perchlorate-containing solutions. Compared to the synthesis of nitrate compounds, perchlorate compounds posses better solubility.

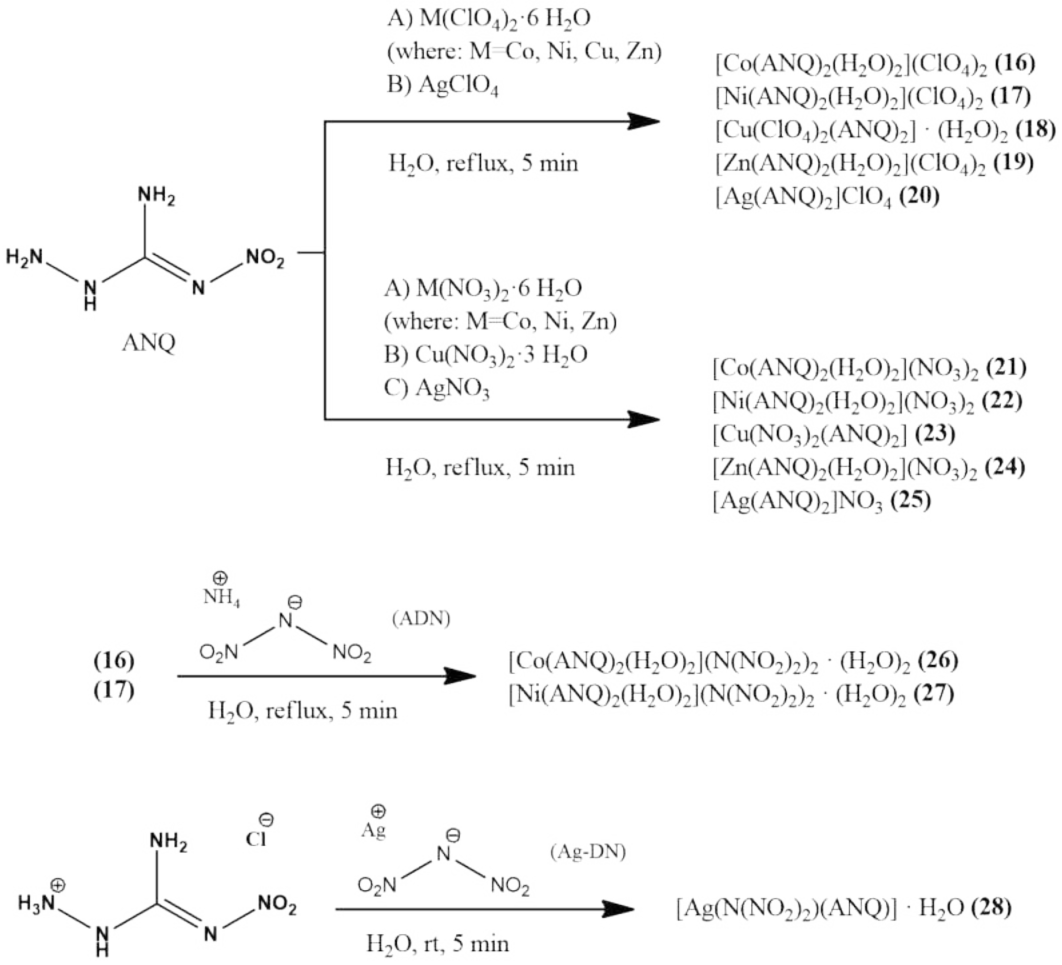


Figure 8: Scheme of formation of energetic coordination compounds containing ANQ ligand and perchlorates and nitrates analogues.

The following table shows selected properties of ECCs containing ANQ ligand (Tab. 3) [98].

Table 3: Results of tests performed for energetic complexes containing ANQ [98].

Compound	**IS [J]**	**FS [N]**	**ESD [J]**	**T $_{\text{dec.}}$ [°C]**
16	3	10	0.03	176
17	3	10	0.04	230
18	< 1	16	0.50	134
19	3	28	0.30	198
20	< 1	< 5	0.01	148
21	9	80	0.70	139
22	4	120	0.08	186
23	< 1	< 5	0.50	77
24	5	120	0.50	181
25	< 1	< 5	0.01	142
26	5	80	0.70	118
27	3	80	0.60	142

From the data presented in the table (Tab. 3), it can be seen that ANQ-based coordination compounds containing nitrates of the corresponding metals have a lower sensitivity values to mechanical stimuli.

Recently, three new derivatives of 1-amino-2-nitroguanidine, substituted with nitroaromatic groups, have been reported - 1-(2,4-dinitroanilino)-2-nitroguanidine (DNNG), 1-(2,4,6-trinitroanilino)-2-nitroguanidine (TNNG) and 1-amino-2-nitroguanidine-3,5-dinitrosalicylic salt (ANQ·DNS) [99]. In relation to 1-amino-2-nitroguanidine, which has a nitrogen content of 58.8 wt. % nitrogen, the nitrogen contents of the three derivatives are noticeably lower and in the range of 32.1 - 34.4 wt. %. The lower nitrogen contents would be expected to generally stabilise the derivatives, but this appears not to be the case, as evidenced by the observed decomposition temperatures of the derivatives being lower by at least 20 °C than the decomposition temperature of the parent molecule. In terms of predicted detonation parameters, although three derivatives have yields exceeding that of 2,4,6-trinitrotoluene (TNT), all fall short of that of RDX, of 1-amino-2-nitroguanidine or of both compounds, but this is yet to be verified experimentally. The only observed improvement in comparison to the parent molecule is that the dinitrosalicylic derivative is virtually insensitive to impact (> 40 J, compared with 20 J for 1-amino-2-nitroguanidine). An alternative approach to the use of guanidine derivatives is to develop their salts with other energetic species, as in the case of the reported di(triaminoguanidinium)-3-nitramino-4-(3-(dinitromethanidyl)-1,2,4-triazol-5-yl)furazanate (DNDTF) [100]. The Authors have synthesised a sequence of similar salts, with the abovementioned DNDTF exhibiting the most favourable properties, e.g. low impact (17.4 J), friction (240 N) and electrostatic discharge (> 225 mJ) sensitivity, as well as acceptable thermal resistance (decomposition temperature of 185 °C. Although the salt was found to be able to initiate a RDX charge (60 mg of DNDTF and 500 mg of RDX) in a lead plate test, when the RDX was substituted entirely by the salt

(560 mg of DNDTF). The perforation of the lead plate was significantly lesser than in the case of a DNDTF/RDX charge, despite DNDTF being predicted by the Authors to have similar detonation properties to RDX. DNDTF can be considered "green" and is an interesting candidate for replacing LA and LS. Nevertheless, one significant drawback that needs to be noted and maybe addressed, is that the synthesis of DNDTF is rather complex, consists of multiple steps and requires the use of relatively sophisticated raw materials, which would be issues when replicating it on an industrial scale.

Energetic coordination compounds containing 3-amino-1-nitroguanidine as a ligand can also contain an azide N_3^- anion. Wang et. al. obtained two coordination compounds $Ni(ANQ)_2(N_3)_2$ and $Co(ANQ)_2(N_3)_2$ [101]. Authors indicate, that these compounds exhibit thermal stability up to 185 °C and 178 °C, respectively, and also have a relatively high sensitivity to impact. For the compound with Ni it is 1.5 J, for the compound with Co it is 4 J. The friction sensitivity is equal to 64 and 72 N, respectively. The obtained ECCs were tested for their use as explosive initiators. For this purpose, a hot stimulation test was carried out in which a small amount of material is placed on a dedicated operating table and then a thermal stimulus (usually a hot needle) is applied. From this, it is possible to assess whether the compound is capable of deflagration or detonation. The study indicates that both compounds obtained containing Ni as well as with Co, undergo deflagration (20 mg of the compound). The authors of this paper also determined the explosion temperature, obtaining 211 and 197 °C, respectively. With regard to testing the possibility of using these compounds in detonators as initiating materials, their initiating ability was tested with regard to RDX (hexogen). A series of detonators for lead plate test were prepared in which 200 mg of the corresponding coordination compound and 450 mg of RDX were used. In the case of the Co-containing compound, full detonation of the hexogen was not observed.

The use of ligands in energetic coordination compounds in the form of guanidine derivatives, as well as various metal ions, makes it possible to obtain compounds with diversified molecular functionality depending on the application required [102]. An example is the preparation of copper-containing catalysts used for atom transfer radical polymerization (ATRP) [103]. The literature indicates that guanidine derivatives may contain additional moieties such as pyridine or quinoline [104]. A major advantage of molecules containing guanidine derivatives, is their multifunctionality, since it is possible to form compounds containing Cu occurring at different oxidation levels - Cu(I), Cu(II) or even Cu(III), which in turn affects the stability of the molecule. In order to improve chemical stability, a benzyl group, for example, can be introduced into the TAG ligand. In the literature one can find ECCs containing triaminoguanide (TAG), which can act as a ligand or cation. However, in the reaction a Cu(II) ion, this ligand is oxidised to form energetic coordination polymers (ECPs) [105].

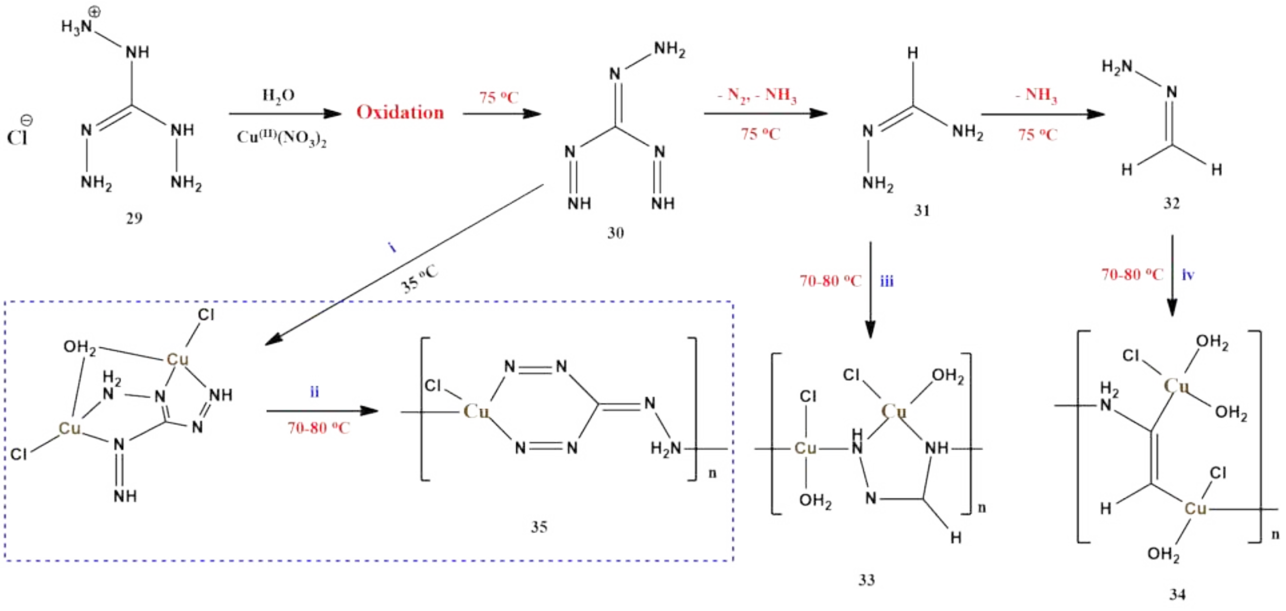


Figure 9: Schematic of in situ TAG oxidation synthesis promoted by Cu(II) and coordination reactions between HAMBDA, FHAA and MHA and CuI ions, resulting in the formation of the corresponding ECPs.

The authors of this paper indicate that the synthesis of coordination energetic polymers **(33)**, **(34)**, **(35)** (Fig. 9, is possible by changing the concentrations of the reactants used (molar ratio of the reactants) and also by modifying the reaction temperature. The synthesis of **(32)** and **(34)** consisted of introducing into an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$, an aqueous solution of **(29)** and then stirring at 65 - 75 °C for 2 h. The difference for the synthesis of the **(35)** compound was the stirring of the reaction mixture at 70 - 80 °C, while for the TAG-Cu(I) complex it was 25-35 °C. Various TAG/Cu(II) molar ratios were also implemented. For reactions i and ii, the ratio was 1:1 (dilute and saturated solutions), while for reactions iii and iv, it was 1:1 and 1:3 (dilute solutions), respectively. The saturation of the solutions affected the structure of the compounds obtained. For the dilute one, spherical structures were obtained, while for the saturated solutions, the obtained compounds exhibited 2D flake structures. The study also indicated that for all the obtained compounds, the nitrogen atom present in the molecule is coordinated with Cu(I), and the water molecule is attached to the ligand. In order to determine the applicability of these compounds as initiating/secondary explosives, the basic safety and detonation parameters were determined. The results are shown in the following table (Tab. 4) [105].

Table 4: Sensitivity and detonation parameters for TAG coordination energetic polymers.

Compound	ρ **[g/cm^3]**[a]	**IS [J]**	**FS [N]**	**D [m/s]**[b]
29	1.55	25	230	7198
TAG-Cu(I) complex	3.01	36	> 360	3783
33	3.08	> 98	> 360	5557
34	3.12	> 98	> 360	5927
35	3.14	> 98	> 360	8969

[a] ρ: measured by helium-gas pycnometer

[b] D: detonation velocity calculated by Explo-5 software

The higher density of the obtained compounds (above 3 g/cm^3) is explained by the high spatial packing and high copper content in the molecule (more than 30 %). It was also noted that the greater the CuCl content in the molecule, the lower the calculated detonation velocity. In addition, the compounds obtained by the authors of the paper, do not exhibit high sensitivity to impact and friction, which may be the reason for the stiffer skeletal structure and the occurrence of a smaller number of crystal defects.

Carbohydrazide

Another example of ligand used in the energetic coordination compounds is carbohydrazide (CHZ) (Fig. 2 structure 8). This compound possesses strong reducing properties and in a coordination compound serves as reducing agent when coordinated simultaneously with a metal ion and oxidising groups. This properties allows to react simultaneously with metal ions and oxidation groups. The literature indicates that the CHZ ligand in perchlorate ECCs can coordinate in two ways. In the first case through carbonyl O atoms and amine N atoms, resulting in a five-membered ring. Coordination by terminal nitrogen atoms is also possible, forming a six-membered ring [106]. CHZ possesses 62.19 wt. % nitrogen and in addition oxygen atom in its structure and its considered as a monodentate or multidentate ligand. Due to the presence of free electron pairs on nitrogen atoms, CHZ can coordinate with the metal atom via the two amino N atoms. Moreover, the chelating effect of the ligand increases their stability [107]. In the literture, energetic coordination compounds containing carbohydrazide ligand are know. They exhibit good detonation properties and high thermal stability and may be used as primary explosives, in gas generators (producing light gases), propellants and pyrotechnic compositions (burn-rate modifiers) [108–111]. An examples of tris(carbohydrazide)metal(II) perchlorates are $M(CHZ)_3(ClO_4)_2$, in which M=Mn, Co, Ni, Zn and bis(carbohydrazide)metal(II) perchlorate, where M correspond to Cu. The ability to coordinate by metal ion with the two or three CHZ ligands is possible through the terminal nitrogen atoms [112]. One method for obtaining carbohydrazide is a one-step reaction between dialkyl carbonate and excess hydrazine [113].

Another way to synthesise CHZ is a reaction of dimethyl carbonate (DMC) and hydrazine hydrate, which is employed in excess. In the first step of the synthesis, methyl hydrazinoformate is formed as an intermediate product, and the resulting methanol is removed from the reaction system. After removing the methanol, the resulting intermediate product reacts with excess hydrazine hydrate to give CHZ [114]. In turn, synthesis of abovementioned compounds is possible by direct reaction of an aqueous solution of metal(II) perchlorate with carbohydrazide in hot ethanol solution 70 °C, what was shown in the Fig. [115].

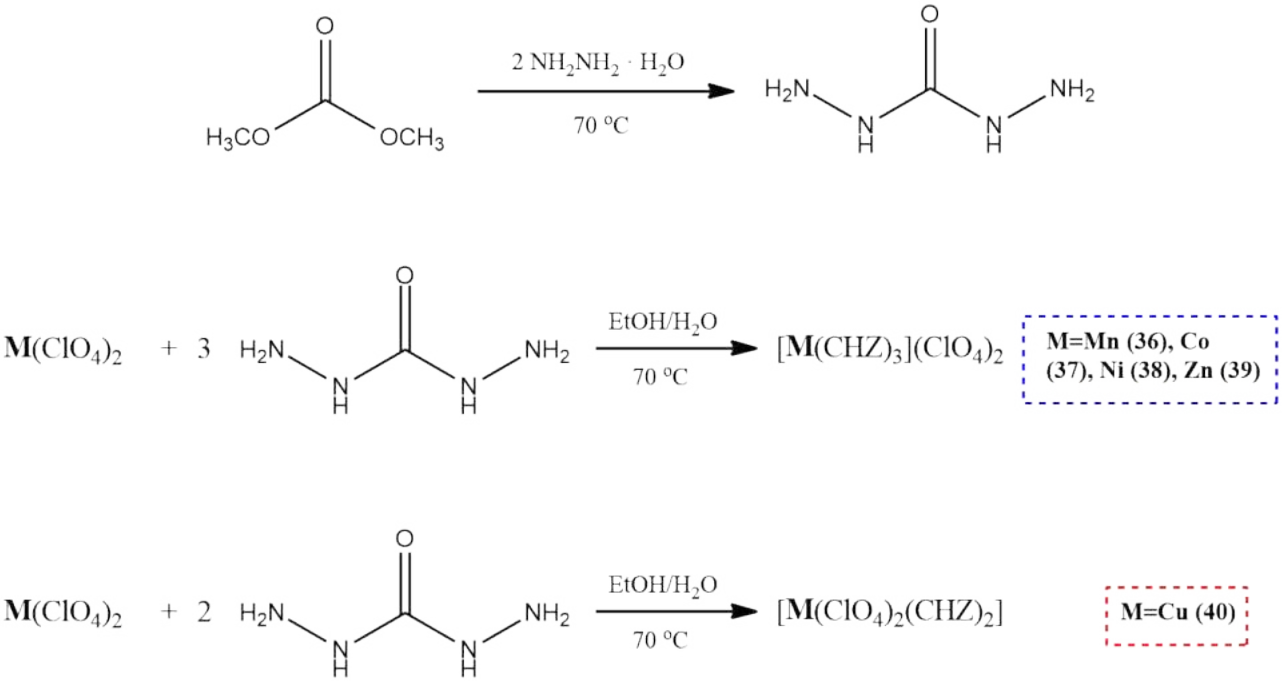


Figure 10: Reaction scheme for obtaining coordination compounds containing a ligand in the form of a carbohydrazide [114, 115].

Selected properties of ECCs containing CHZ ligand are presented in the Table 5 [115].

Table 5: Properties of energetic coordination compounds containing tris- and bis(carbohydrazide)metal(II) perchlorates.

Compound	IS [J]	FS [N]	ESD [J]	T_{dec} [°C]
36	2	24	0.50	263
37	1	≤ 5	0.035	243
38	1	≤ 5	0.30	273
39	1,5	20	0.70	268
40	3	< 5	0.02	186

All the compounds indicated in the table above, are characterised by high sensitivity to friction, impact as well as electrostatic discharge. However, they exhibit good thermal stability, their thermal decomposition temperature being above 240 °C, unlike $[Cu(ClO_4)_2(CHZ)_2]$, which decomposes at 186 °C.

The literature also indicates that in energetic coordination compounds, the ligand function can also be performed by carbohydrazide derivatives. It is equally feasible to combine carbohydrazine groups with a nitrogen-rich heterocyclic compound such as furazane and $Cu(ClO_4)_2$ to obtain initiating compounds [116]. The figure (Fig. 11) indicates the possible coordination sites for the selected compounds/groups (path 1) indicating that the 0D structure may be obtained, in the compounds it is not possible to introduce multiple oxidative groups into the molecule [32].

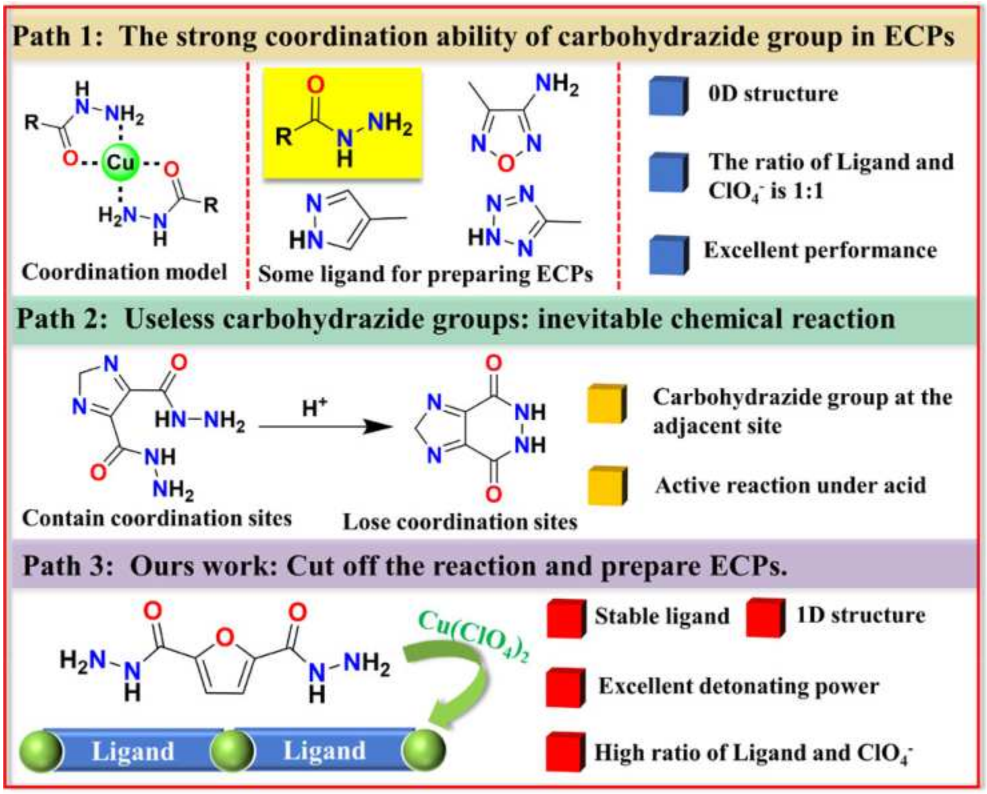


Figure 11: Coordination site about skeletal and substituent in energetic materials [32].

In order to achieve improved detonation parameters, it is preferable to select heterocyclic, organic ligands in which CHZ can be a substituent. In the design/synthesis of new compounds, it should also be considered that CHZ groups as substituents should not be neighboring each other (path2), since they may lose hydrazine to form a diazine ring (lack of coordination ability), and, above all, undergo a cyclization reaction, resulting in the formation of a more active and stable ring [117].

There are also iron-containing ECCs - iron(II) carbohydrazide perchlorate, $[Fe^{II}(CHZ)_3](ClO_4)_2$, in which the iron ion is coordinated with three carbohydrazide molecules to form a six-coordinated complex cation [118]. This compound, compared to other compounds containing carbohydrazide and perchlorates of Co, Ni, Cu and Zn, are characterised by greater sensitivity to mechanical stimuli and lower thermal stability. Thermal decomposition of the compound occurs at temperatures below 200 °C (about 153 °C). In the case of iron-containing compounds, it is important to determine the stability of the compound, which gives information about the safety of handling, especially in the context of the use of compounds with iron in the military industry (weapons). $[Fe^{II}(CHZ)_3](ClO_4)_2$ can be obtained by a multi-step reaction, as shown in the figure below (Figure 12). In the first stage, a solution of NaOH is dropped into a solution of $FeCl_3$, obtaining iron(III) hydroxide. In the next step, the resulting precipitate is dissolved in a solution of $HClO_4$, obtaining $Fe(ClO_4)_3$. Then into an aqueous solution of carbohydrazide, ferric perchlorate is introduced at an elevated temperature (65 °C). The target compound was obtained by slow evaporation of the solvent.

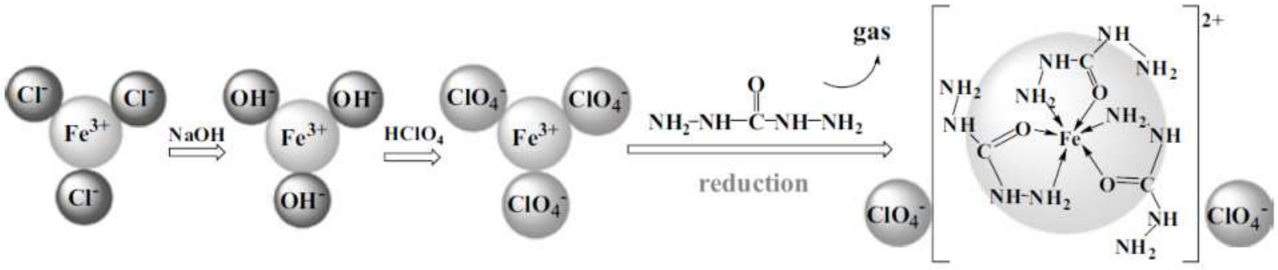


Figure 12: Synthesis route of Fe-based CHZ complex.

Structural studies indicate that $[Fe(CHZ)_3](ClO_4)_2$ exhibits a monoclinic crystalline system. Considering the sensitivity parameters, impact sensitivity, the 50 % firing height was 9.5 cm. Friction sensitivity was determined using a pendulum apparatus, which resulted in a firing rate of 98 % for FeCP. The study also shows that high impact sensitivity, is associated with a smaller energy gap (HOMO-LUMO). The smaller the energy gap value, the higher the sensitivity. Gilman confirmed that [119] is related to the detonation process, because as a result of the first stage of detonation, there is an electron excitation from the HOMO orbital to the LUMO orbital and consequently a bond break between the metal and the ligand.

An example CHZ derivative ligand might be furan-2,5-dicarbohydrazide (FDCA), which synthesis was described in the work [32] (reaction of dimethyl furan-2,5-dicarboxylate with hydroxylamine hydrate). The authors of this work, synthesised coordination compound as $[Cu(FDCA)(H_2O)ClO_4]_n(ClO_4)_n \cdot nH_2O$ (ECPs-1$\cdot$ nH_2O). The work indicates that the compound is thermally stable, and its most important feature is that it exhibits a detonation capacity comparable to that of lead(II) azide. However, the successful synthesis of ECPs-1$\cdot$ nH_2O coordination compound was enabled by isolating the position of the carbohydrazide groups, and as a consequence, the site of occurrence of the chemical reaction was also switched, without resulting in a spherical valve. Considering the sensitivity parameters of the indicated compound, the friction sensitivity is 0.1 N, the impact of 2 J, making this compound high sensitiv to simple stimuli. Moreover, the calculated detonation velocity of ECPs-1$\cdot$ H_2O is equal 7600 m/s, which is much greater value in comparison for LA [32].

Another example of the modification of the CHZ ligand molecule is the preparation by the authors of the paper [35] of the ligand 1H-pyrrole-2-carbohydrazide (PRCA), consisting of a low-nitrogen pyrrole and a hydrazide group, and then obtaining the energetic coordination compound $[Cu(PRCA)(H_2O)(ClO_4)]ClO_4$. The same authors in their other work also presented ECCs in the form of $Cu(TZCA)_2(ClO_4)_2$ **(42)**(where: TZCA - 1H-tetrazole-5-carbohydrazide) [120], $Cu(AOCA)_2(ClO_4)_2$ **(43)** (where: AOCA - 4-amino-1,2,5-oxadiazole-3-carbohydrazide) [121] and $Cu(PZCA)_2(ClO_4)_2$ **(44)** (where: PZCA - 1H-pyrazole-4-carbohydrazide) [122]. The synthesis of the PRCA-containing compound involved preparing a suspension of the ligand in ethanol and then slowly adding $HClO_4$ until a clear solution was obtained. After heating the solution to 50 °C and then filtering, $Cu(ClO_4)_2 \cdot 6H_2O$ was added. When the solvent was evaporated, the obtained compound was dried for 5 h at 50 °C. The energetic properties of the obtained compounds are summarized in the following table (Tab. 6).

Table 6: Energetic properties of ECCs containing CHZ ligand derivatives [35].

Compound	ρ **[g/cm³]**	$T_{dec.}$ **[°C]**	**IS [J]**	**FS [N]**	**D [m/s]**[a]
41	1.83	219	7	16	6200
42	1.92	177	< 1	7	7945
43	2.01	170	4	30	7400
44	1.84	200	1	5	6776

[a] D: detonation velocity calculated by Explo-5 software

The compounds showed high detonation parameters and high sensitivity to mechanical stimuli, which was unfavorable for further application. Wang's group also investigated the sensitivity of **(41)** to laser light initiation. It turned out that the compound detonated at a laser energy of 80 mJ. In order to determine the detonation performance, a lead plate damage test was also carried out using ECCs-1 as the initiating material (30 mg) and RDX as the secondary explosive (300 mg). The result obtained indicated that the compound can fully detonate RDX, the thickness of the broken lead is 3 mm, and the diameter of the hole reaches 22 mm.

A further example of a recently obtained ligand is 1H-imidazole-4-carbohydrazide (4-IMCA), from which the cooordination compound $Cu(4\text{-}IMCA)_2(ClO_4)_2$ containing copper(II) perchlorate was synthesised [123]. The synthesis of 4-IMCA involved the reaction of methyl 4-imidazole carboxylate with methanol and the subsequent addition of hydroxylamine hydrate at room temperature. After the reaction was completed, the reaction mixture was placed in a refrigerator, which allowed the separation of compound crystals. To obtain the coordination compound, an aqueous solution containing 4-IMCA was prepared, to which $HClO_4$ was introduced after heating to 45 °C, followed by methanol and then $(ClO_4)_2 \cdot 6H_2O$. After filtering the reaction mixture, the resulting filtrate was evaporated to obtain the target coordination compound (Fig. 13).

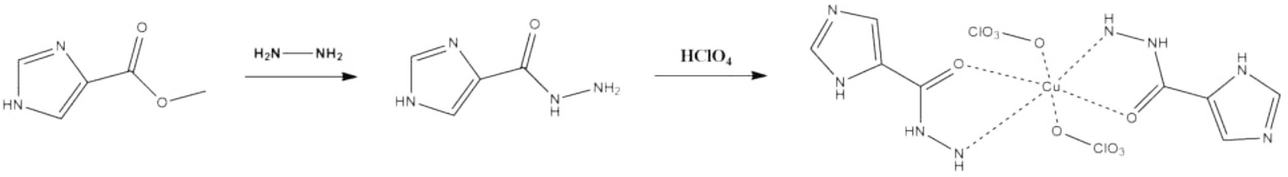


Figure 13: Synthesis scheme of $Cu(4\text{-}IMCA)_2(ClO_4)_2$.

The resulting coordination compound has a high density of 1.975 g/cm$_3$. The results obtained by the authors of the paper indicated that the compound has good thermal stability - exothermic decomposition occurred at 218 °C. In addition, the safety parameters of $Cu(4-IMCA)_2(ClO_4)_2$ indicate that the impact sensitivity is 3 J, while the friction sensitivity is 7 N. Compared to the values for lead(II) azide, this compound can be regarded as insensitive. Wang's group also determined the detonation parameters, indicating that the calculated detonation velocity was 7100 m/s and the detonation pressure was 23.5 GPa. In addition, initiation capacity tests (hot-ignition test, laser ignition test, lead plate initiation test) were conducted in an attempt to initiate RDX. It was indicated that 40 mg of the coordination compound results in the full detonation of 500 mg of RDX, so $Cu(4-IMCA)_2(ClO_4)_2$ may be considered as potential replacement for LA.

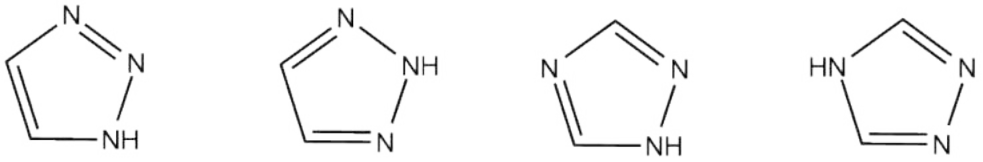
Besides carbohydrazide, the literature also indicates the use of semicarbazide (SCZ) and and methyl carbazate (MCZ) as ligands [19]. SCZ compound contain five-membered ring with oxygen and a terminal nitrogen atom. Numerous works have been produced with semicarbazide as a ligand and central metals such as nickel, cadmium and zinc [118, 124, 125]. Examples of such a compound are $[Ni(SCZ)_3](NO_3)_2$ and $Cu(SCZ)_2Cl_2$, for which coordination results in a five-membered ring [126]. SCZ is a bidentate ligand, which can coordinate to the central cation Ni or Co with an oxygen atom derived from the carbonyl group and a nitrogen atom of the hydrazine group. Examples of methyl carbazate containing compounds are $[Co(MCZ)_3](NO_3)_2 \cdot H_2O$ and $[Ni(MCZ)_3](NO_3)_2 \cdot H_2O$ [127, 128]. The literature indicate, that MCZ-based compounds has found applications in the production of drugs pesticides and petroleum derivatives. In coordination chemistry, it functions as a ligand chelating agent [129]. The work [19] reported the synthesis and thermal as well as energetic properties of zinc nitrate coordination compounds $[Zn(SCZ)_3](NO_3)_2$ **(45)**, $[Zn(CHZ)_3](NO_3)_2$ **(46)**, $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ **(47)**, verifying whether there is an influence of the type of ligand on properties, for structurally similar compounds. Based on the crystallographic data, all compounds exhibited a monoclinic crystal system and also possessed three five-membered rings. The compounds have a high density of 1.901 g/cm^3, 1.859 g/cm^3 and 1.743 g/cm^3, respectively. From the point of view of energetic parameters, the higher the density of the compound, the better the detonation performance, as can be observed for the compound containing SCZ. The high density is attributable to the presence of an uncoordinated amine group, which is partially dissociated and, compared to a hydrazine or methoxy group, is the smallest group. In addition, in the molecule, the presence of hydrogen bonds in addition to coordination bonds, affects the formation of multidimensional supramolecular structures that provide good thermal stability (exothermic decomposition above 300 °C). Considering the sensitivity parameters, the compound containing semicarbazide showed the lowest sensitivity to impact and friction. In the case of impact sensitivity, for the compound containing CHZ, 50 % of the firing height was 50 cm, while for the others it was 0 % (compounds insensitive to impact). In contrast, in the case of friction sensitivity, for the compound containing MCZ, 50 % of the firing height was 20 cm, while the remaining specimens displayed no sensitivity.

3.4. ENERGETIC COORDINATION COMPOUNDS CONTAINING HETEROCYCLIC LIGANDS

Among researchers, the field of new energetic materials is being increasingly developed, with particular emphasis on nitrogen-rich compounds. The introduction of modifications of currently existing compounds makes it possible to obtain new materials that are safer in use and exhibit high detonation parameters. Such a group of compounds are heterocyclic compounds with N−N and N=N bonds [130]. The ability to reduce the sensitivity of compounds to mechanical stimuli or to provide greater thermal stability may be due to the exhibiting of aromaticity and conjugation effects [131]. Examples of the heterocyclic ligand incorporated into energetic coordination include are for example triazoles, tetrazoles, oxadiazoles and its derivatives [132, 133].

Triazoles and their derivatives

Commonly used ligands in energetic coordination compounds are triazoles and its derivatives. Triazoles are heterocyclic compounds, built from a five-membered ring containing three nitrogen atoms in its structure (60.84 wt. % nitrogen). They can occur in the form of four isomers: 1H-1,2,3-triazole **(48)**, 2H-1,2,3-triazole **(49)**, 1H-1,2,4-triazole **(50)** and 4H-1,2,4-triazole **(51)** (Fig. 14) [134]. Occurring in the aromatic ring of triazole, three conjugated nitrogen atoms allow to obtain high thermal and chemical stability and ensure high enthalpy of formation [135]. 1,2,3-triazoles have a higher enthalpy of formation of 240 kJ/mol, in contrast to 1,2,4-triazoles (182 kJ/mol), which is why they are more often chosen for the synthesis of new compounds [136]. Due to the presence of three nitrogen atoms in the structure that serve as electron pair donors, it is possible to form multicore compounds in which the ligand molecule links coordination centers. For compounds containing 1,2,4-triazole, the ligand is coordinated by the metal at positions 1 and 2 to form "coordination polymers".



48 49 50 51

Figure 14: Triazole isomers.

Considering the geometry of coordination compounds, the triazole ring is involved in hydrogen bonding due to the presence of an active hydrogen atom in the ring, which is bonded to one of the nitrogen atoms. Moreover, the ring may acts as a hydrogen acceptor due to the presence of one of its lone electron pairs on nitrogen atom, thus affecting the geometry of the compounds [134].

Arrangement of nitrogen atoms in different positions in the ring, allows the ligand to combine with different metal anions. As a result, a bridge may be formed, which has a varied geometry depending on the properties of the metal and the donor atoms. The most common coordination mode for triazole compounds is the N1, N2 bridging mode, with a substituted N4 position. In this case, two metal ions are close to each other at a distance of about 400 pm by the first bridging ligand. Therefore, the presence of two more ligands in the molecule having negative charges is crucial to reduce or prevent the repulsion effect of the two metal ions [137]. When large substituents at positions 3 or 5 are present in the molecule, the third ligand may be replaced by a smaller bridging anion such as F^- [138] or NCS^- [139]. In some cases, due to the large size of the bridging anions, only one triazole bridge may be present, except for two bridging anions, as in multinuclear compounds. Examples of such a compound include $[Cu(Htrz)Cl_2]$ and $[Cu(Htrz)Br_2]$ (Htrz-1,2,4-triazole) [134]. For the presence of a triple triazole bridge N1, N2 in the molecule, the metal ions are on the trigonal axis. For 4-substituted triazole coordination compounds, this geometry is the most common. Taking into account the bridging mode of N2, N4 triazoles, the metal ions are close to each other at a distance of about 650 pm. Coordination compounds $[M(Htrz)_2(NCS)_2]$, where M: Cr, Mn, Fe, Co, Ni, Cu, Zn are two-dimensional compounds [134]. An example of this kind of compound is shown in the figure (Fig. 15).

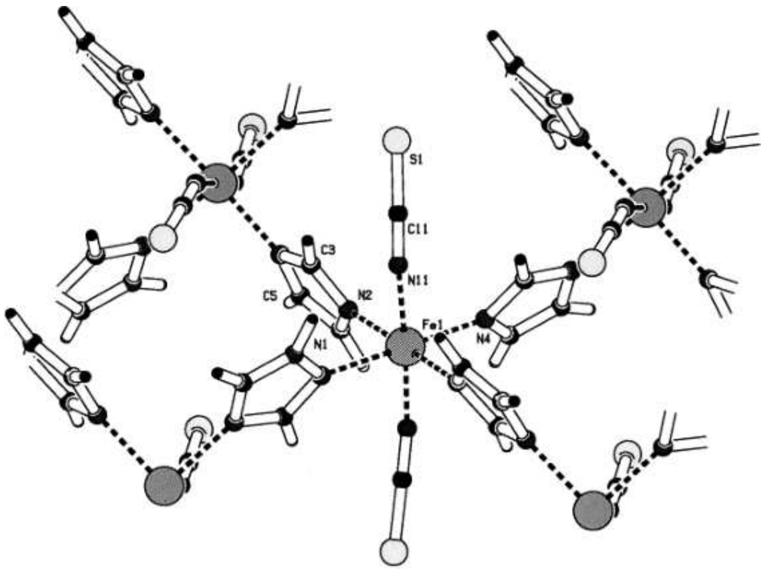


Figure 15: Examples of two-dimensional structure of $Fe(Htrz)_2(NCS)_2$ [134].

However, for providing better detonation performance of ECCs, it is advantageous to use N1-substituted aminotriazoles than unsubstituted compounds.

There are also triazole derivatives, which contain various substituted functional groups. The Fig. 16 shows triazole derivatives **(34-40)**, which were arranged with increasing amounts of nitrogen in the molecule respectively: 44.03; 49.12; 54.26; 66.64; 70.67; 73.65 wt. %.

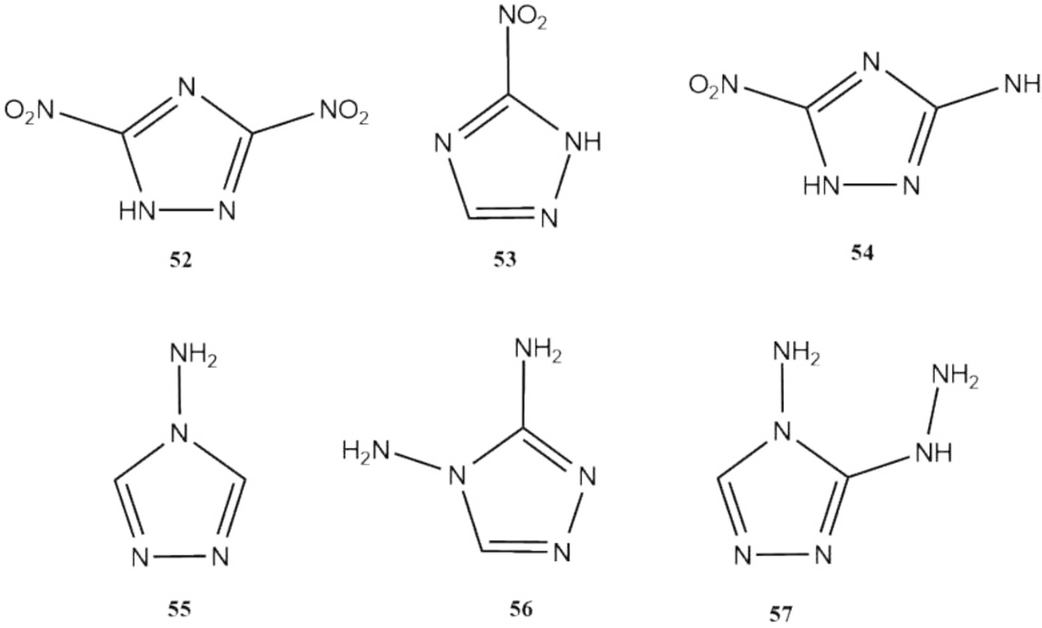


Figure 16: Triazole derivatives.

Triazoles compounds can be combined with energetic substituents such as nitro $-NO_2$, nitrato $-ONO_2$, nitramine -$-NHNO_2$ and nitroimine $=NNO_2$ [140]. However, regardless of the type of compounds, energetic materials should exhibit certain features. Besides their low sensitivity to mechanical stimuli (friction, impact, shock), high thermal stability, high density and, above all, their attainment of high detonation parameters (velocity, pressure), they should posses a high heat of formation and a positive oxygen balance. For example, frequently introduce a nitro group into the ligand molecule (for instance 1,2,3-triazole nitro derivatives), which on the one hand decreases the heat of formation of the compound, but on the other hand increases the density of the compound, improves the oxygen balance and detonation parameters [141]. Improving the oxygen balance by introducing additional NO_3 groups into the molecule, provides a greater number of oxidising units necessary to oxidize the components of the compounds and, consequently, achieve the highest possible energy potential [142].

The literature indicates that there are two approaches to the synthesis of N-substituted 4-nitro-1,2,3-triazoles [143]. The first approach points to the heterocyclization of nitrogen derivatives containing C−C, N−N and C−N bonds [144], in which mainly N3-substituted compounds can be obtained. However, it is not often employed. A second, more conventional approach is the alkylation of unsubstituted 4-nitro-1,2,3-triazoles, which can yield compounds substituted at the N1, N2 and N3 positions in the ring. A major advantage of this method is the ability to change the position of substituents in the structure of nitrotriazoles, influencing on the properties [143]. The alkylation reaction is usually carried out in the presence of alkali-substituted compounds, since under alkaline conditions nitrotriazoles exhibit the nature of ambident nucleophiles. However, the data available in the literature on the alkylation of N-substituted triazoles are limited and indicate that only a mixture consisting of two isomers (N1, N2) is obtained [145]. An example is the synthesis of 4-amino-1,2,3-triazole with propargyl bromide and ethyl iodides. Currently, there is a great interest among researchers related to obtaining and determining the properties of isomers of compounds substituted at the N3 position and their compounds with metal complexes. From a synthetic point of view, such compounds are of interest because compounds substituted at the N3 position are more efficient, compared to others, in quaternization (in t-BuOH–$HClO_4$ system) and complexation reactions [146]. The figure below (Fig. 17) presents the reaction scheme of alkylation.

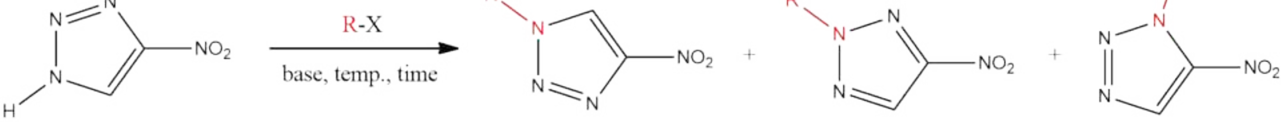
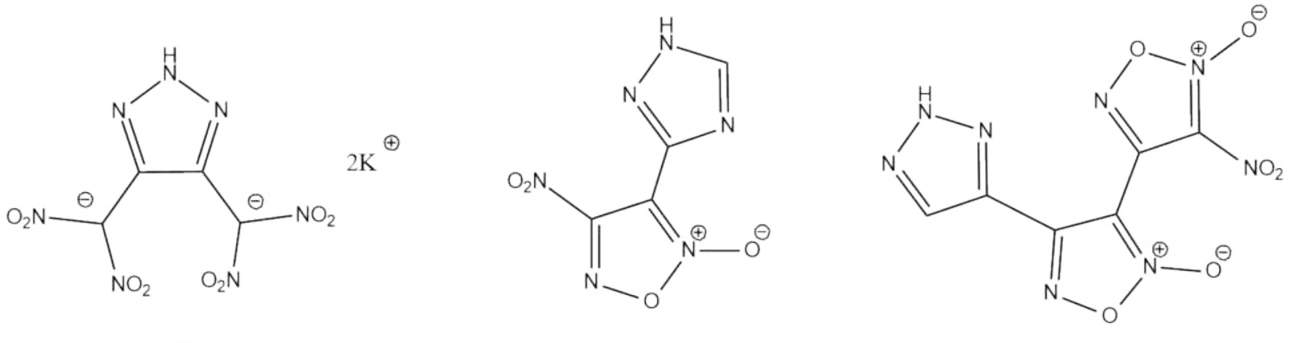


Figure 17: Scheme of alkylation reaction of 4(5)-nitro-1,2,3-triazole with different alkylating agents (where R= Me, Et, n-Pr, i-Pr, n-Bu, i-amyl, Bn, 2-ethylhexyl, cyclohexyl; M= $MeOSO_2$, $EtOSO_3$, I, Br, Cl, ONO_2) [143].

The synthesis of triazoles involves the preparation of a suspension of triazole with ethanol, to which sodium hydroxide and cyclohexyl nitrate were later added in the same molar ratio. The reaction was carried out at 78-80 °C for 13 h. After the reaction mixture cooled to room temperature, the ethanol was evaporated and water was added to the residue and heated to 90-95 °C. The reaction was carried out with continuous stirring for 25 h. Based on 1H NMR investigations, the separated product was found to be a mixture of three isomeric N cyclohexylonitrotriazoles. Based on experiments, the authors of the paper [143] found that all heteroatoms undergo electrophilic attack, regardless of the type of alkylating agent (alkyl or aryl halides, alkyl nitrates, or dialkyl sulfates), the type of solvent used during the synthesis, the type of base and also the temperature and time of the reaction. Each of these variables required adjustment of separate synthesis conditions, e.g. the use of a particular type of alkylating agent determined the ratio of alkylation products. The substituted N3 isomer obtained in the mixture of isomers, in the case of alkylation products of triazole and dialkyl sulfates, accounted for 11-12 %, while when using alkyl halides the content did not exceed 9 %.

Another example of compounds with a substituted nitro group can be those containing a 1,2,3-triazole ring in the structure [147] and also compounds containing a 1,2,4-triazole ring combined with a furoxane ring (Fig. 18) [148].



58 **59** **60**

Figure 18: 1,2,3-triazole and 1,2,4-triazole based energetic compounds (Where **58**: potassium 4,5-bis(dinitromethyl)-1,2,3-triazolate; **59**: 3-(1,2,4-triazolyl)-4-nitrofuroxan); **60**: 1,2,4-triazole-nitrofuroxan hybrid.

The nitrogen content of the indicated compounds is 27.8, 42.4 and 39.7 wt. %, respectively. Due to their good detonation performance, these compounds can potentially be used as lead-free primary explosives. The energy properties of the compounds are summarized in the following table (Tab. 7).

Table 7: Energetic properties of triazole-based compounds.

Compound	ρ [g/cm^3]	D [m/s]	P [GPa]	IS [J]	FS [N]	T $_{\text{dec.}}$ [°C]
58	2.04	8715	28.3	1	60	131
59	1.82	8400	33	50	> 360	138
60	1.59	7600	26	4.4	130	133

The data shows that compound **(59)** is not sensitive to impact and friction, however, it does not exhibit high thermal stability - the thermperature of exothermic decomposition is about 130 °C (similar to that for **(58)** and **(60)**).

The following figure (Fig. 19) shows examples of compounds containing substituted (NO_2, NH_2 groups) pyrazole units as substituents linked to triazole moieties refered as azo-bridged triazoles [149].

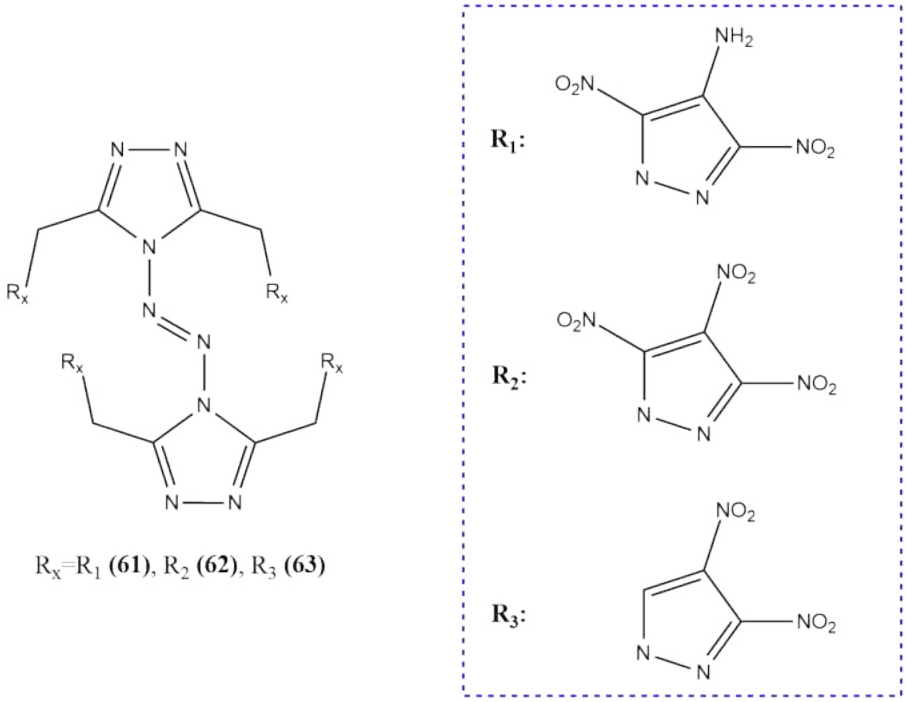


Figure 19: Examples of azo-bridge triazoles with different substituents.

The following table summarizes selected properties of the indicated amine-substituted pyrazoles (Tab. 8) [140].

Table 8: Energetic properties of amine-substituted pyrazoles compounds.

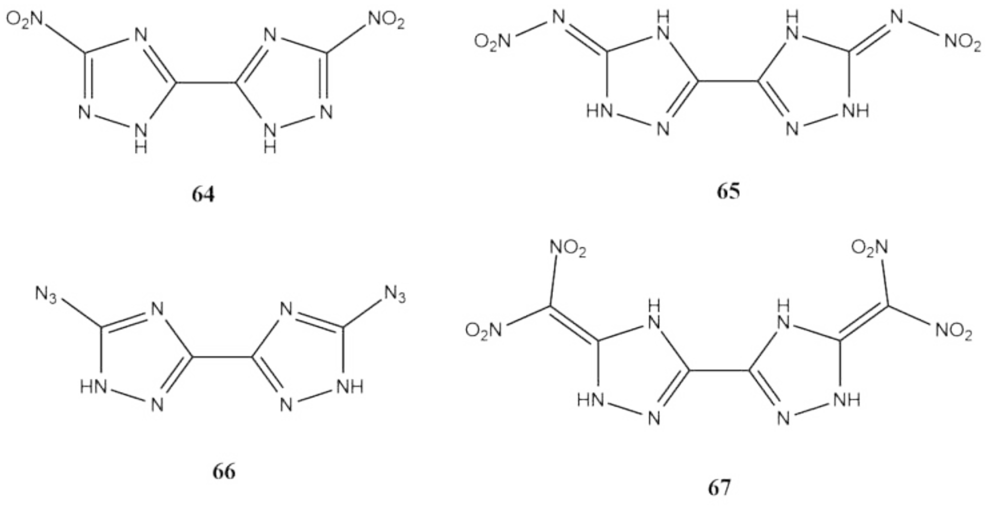
Compound	**D [m/s]**[a]	**P [GPa]**[b]	**ΔH_f [kJ/mol]**[c]	**IS [J]**	**FS [N]**	**T $_{dec.}$ [°C]**[d]
61	8190	27.3	1483.4	36	> 360	-214
62	8637	32.3	1359.0	10	240	-151
63	8068	26.9	1381.8	15	240	-162

[a] Calculated detonation velocity (EXPLO5)
[b] Calculated detonation pressure (EXPLO5)
[c] Calculated molar enthalpy of formation in solid state
[d] Temperature of decomposition (onset)

From the above data, it can be seen that a compound containing an amine substituent has the lowest sensitivity to mechanical stimuli **(61)**. The removal of an amino group in the compound **(63)** promotes the improvement of detonation parameters, however, presence of two nitro groups increases the sensitivity to friction and impact. This trend is maintained, with the attachment of another nitro group to the molecule **(62)**. The literature indicates, in designing new energetic compounds, the authors often introduce a triazole ring into the molecule, enabling an increase in the thermal stability of the compound and therefore lowering the sensitivity to shock and impact. In addition, a higher nitrogen content in the molecule is preferred, which increases the crystal density, causing release more energy as a result of decomposition, providing better detonation parameters [150].

Bis-1,2,4-triazoles bonded through C−C bond

1,2-4-triazoles can be linked together by a C−C bond to form bis-triazoles. Compounds of this type can exhibit similar energetic properties to azo-bridged compounds such as 5,5'-bistetrazoles [151]. The figure below (Fig. 20) shows examples of bis-triazole compounds functionalized with amine, nitro, nitramine, azide and dinitromethyl groups [152].



64

65

66

67

Figure 20: An example of bis-triazole ligands.

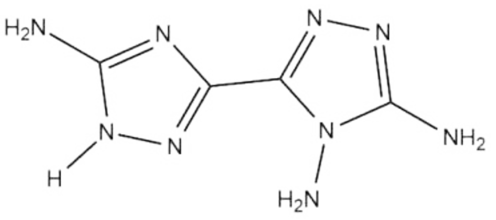
For all compounds containing bis-triazole moiety plannar arrangement can be observed. Based on the data from XRD analysis, compounds **(64)** and **(65)** crystallize in monoclinic space group and **(66)** crystallize in triclinic space system. The authors of this work do not indicate space group for **(67)**. Within molecules, there are hydrogen bonds involving nitrogen atoms in the triazole ring, and intermolecular interactions are also present, such as those originating from oxygen atoms in the nitro group. The authors of the study also determined a number of physicochemical as well as energetic properties which were shown in table below (Fig. 9):

Table 9: Physiochemical and calculated eneregtic parameters for bis-triazole compounds [152]

Property	**64**	**65**	**66**	**67**
ρ [g/cm^3]	1.90	1.80	1.70	1.95
$T_{dec.}$ [°C]	251	194	201	121
IS [J]	10	3	3	20
FS [N]	360	108	48	360
ESD [J]	0.1	0.5	0.04	0.2
P [kbar]	320	300	250	341
D [m/s]	8413	8355	7944	8499

The compound containing an azide group (DAzBT) has the highest nitrogen content in the molecule. Of the compounds indicated in the table, it shows the highest sensitivity to mechanical stimuli and sensitivity to electrostatic discharge, as does DNABT. DNBT, on the other hand, exhibits insensitivity to friction and negligible sensitivity to impact, while it has high thermal stability (over 250 °C). An advantageous solution from the point of view of achieving the best detonation parameters (pressure and detonation velocity) turned out to be the introduction of dinitromethyl groups into the bis-triazole molecule (DNMBT). Due to its low thermal stability (121 °C), its use in the formation of new compounds is limited.

An example of a compound containing bis(triazole) may be 1H,4'H-[3,3'-bis(1,2,4-triazoles)]-4',5,5'-triamine ($C_4H_7N_9$), containing 69.6 wt. % nitrogen. The compound is versatile, as it is basic-acid in nature and has three amine groups. As such, it can accept up to two protons, forming a monocation or dication, but can also donate one proton, forming an anion. The authors of the paper [36] determined the effect of the obtained compound in neutral form and the salt of the monocation and dication with energetic counter-ions (perchlorate, nitrate, dinitramide) on sensitivity to mechanical stimuli as well as on thermal stability. The following figure shows the different forms of abovementioned forms of compounds (Fig. 21).



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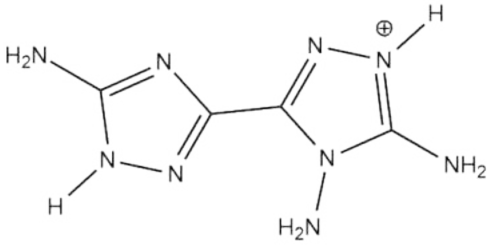

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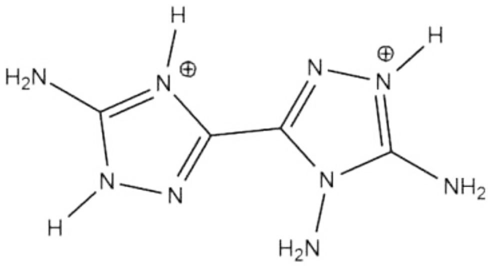

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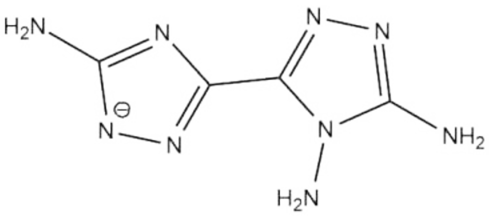

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Figure 21: Different forms of 1H,4'H-[3,3'-bis(1,2,4-triazoles)]-4',5,5'-triamine.

In the work [36] it was determined acid-base equilibria by potentiometric-spectrophotometric titration in sodium chloride medium. On the basis of the dependence of $\lambda_{\max}$ on pH, they indicated that the compounds studied occur in solutions with a specific pH range. The first pH range included values from 0.7 to 2.9, the second from 3.3 to 6.6 and the third from 8.9 to 9.8. Knowing the pH range in which a particular ionic form of a compound occurs, it is possible to crystallize it selectively.

As mentioned above, the authors determined the energetic properties for a number of compounds: neutral form $C_4H_7N_9$ **(68)**; cation $C_4H_8N_9^+$ **(69)**, counter-ion $N_3O_4^-$ **(70)**; dication

$C_4H_9N_9^{2+}$ with counter-ion, ClO_4^- **(71)**, NO_3^- **(5)**, which are shown in the following table (Tab. 10).

Table 10: Sensitivity and detonation parameters for compounds based on 1H,4'H-[3,3'-bis(1,2,4-triazoles)]-4',5,5'-triamine [36].

Compound	ρ **[g/cm^3]**	**$T_{dec.}$ [°C]**	**IS [J]**	**FS [N]**	**ESD [J]**	**D [m/s]**[a]
68	1.599	347	> 40	> 360	1	7681
69	1.803	230	4	> 360	0.1	8948
70	1.873	270	4	192	0.1	7033
71	1.740	210	> 25	> 360	0.6	8092

[a] Calculated detonation velocity

The data shows that the neutral compound is insensitive to friction and impact and is thermally stable compared to its salts. In contrast, the compound containing the perchlorate anion has the highest sensitivity to mechanical stimuli. Taking into account the indicated properties of the salts, they may find application as propellant charges or as gas generators.

An interesting example of triazole derivative is 5-amino-1H-1,2,4-triazole-3-carbohydrazide, using which, the authors of the paper [153] obtained a number of energetic compounds. Due to the high nitrogen content of the molecule, resulting from the presence of several amine groups, it is advantageous to combine the cation of this compound with an anion containing either nitro or nitramine groups. As a consequence, it would be possible to form more intramolecular and intermolecular hydrogen bonds, favorably influencing increased thermal stability, higher density and better detonation parameters. The figure below (Fig. 22) shows the structure of energetic salts.

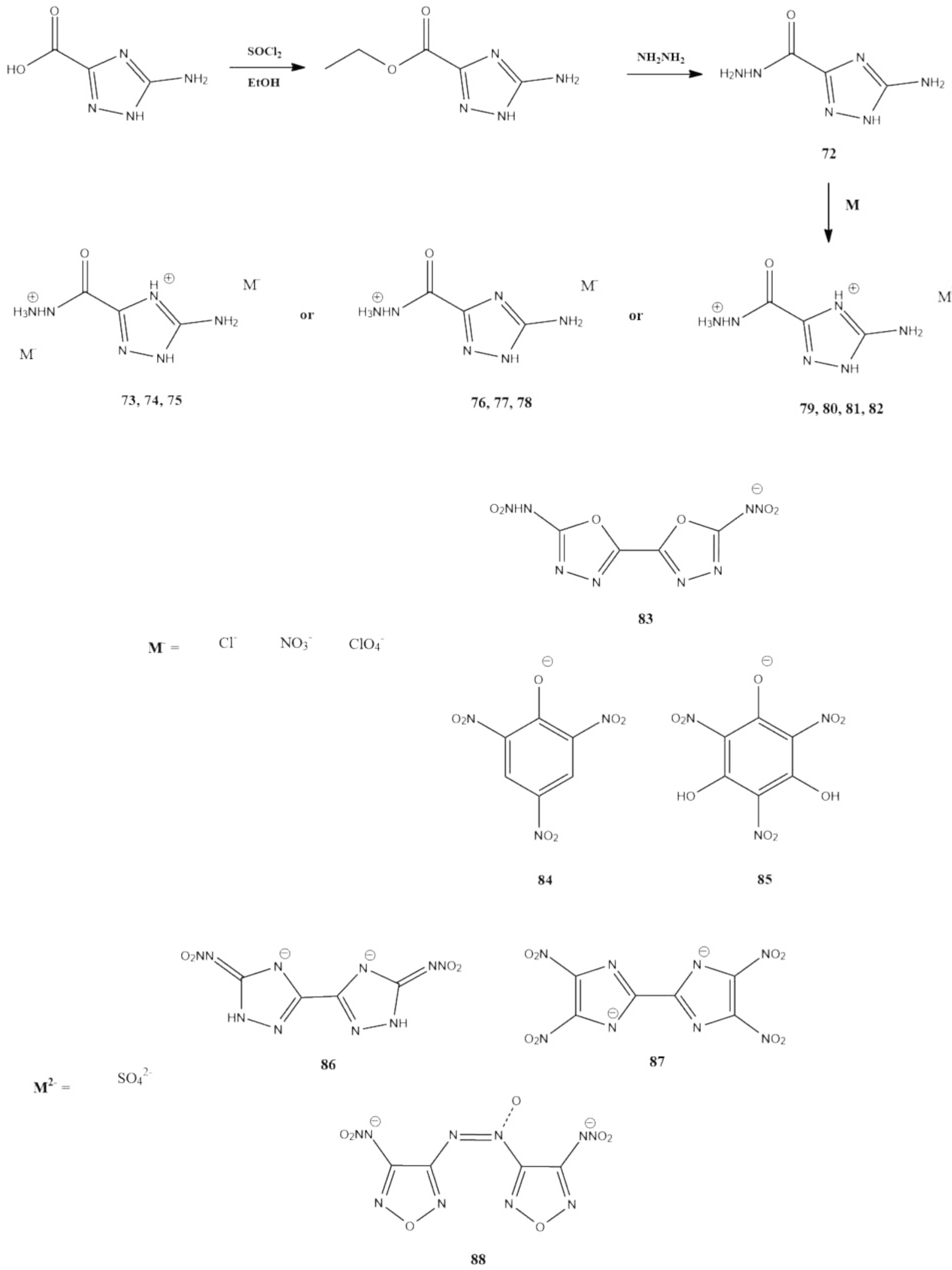


Figure 22: Synthesis scheme of 5-amino-1H-1,2,4-triazole-3-carbohydrazide **1** and its salts.

The crystal structure was characterised for compounds **72, 73, 74, 75, 78 and 79**. All compounds except compound **74** which has a triclinic system exhibit a monoclinic crystal system. In addition, XRD analysis indicated that six types of crystal packing in the molecule are possible, respectively for compounds: **72**: sandwich type, **73**: graphene type, **74**: lamellar type, **75**: interlock type, 78: face-to-face type, and 8: wavelike type. However, the different types have not been characterised in detail to determine their influence on energetic properties.

Also it was determined the physicochemical and energetic properties, which were shown in Tab. below (Table 11).

Table 11: Physiochemical and energetic properties of 5-amino-1H-1,2,4-triazole-3-carbohydrazide and its salts.

Compound	ρ **[g/cm^3]**	**N [%]**	**T$_{\text{dec.}}$ [°C]**	**IS [J]**	**FS [N]**	**P [GPa]**[a]	**D [m/s]**[b]
72	1.70	63.03	401	> 80	360	20.6	8038
74	1.74	33.10	216, 375	> 80	120	25.3	7902
75	1.85	43.73	213, 343	7	168	27.7	8053
76	1.69	48.27	159	10	168	24.0	7943
77	1.72	32.94	241	7.5	144	22.3	7658
78	1.81	30.11	202	18	160	24.9	7902
79	1.80	46.83	259	> 80	324	34.6	9571
80	1.76	46.58	248	11	120	33.5	9193
81	1.63	52.27	204	25	252	33.7	8820
82	1.75	47.01	161	5	120	38.3	9323
RDX	1.81	37.84	210	7.5	120	34.7	8872
HMX	1.90	37.84	279	7	120	39.2	9254

[a] Detonation pressure calculated by Explo-5
[a] Detonation velocity calculated by Explo-5

Among all compounds, the base compound 5-amino-1H-1,2,4-triazole-3-carbohydrazide has the highest nitrogen content in the molecule (63.03 wt. %), compound **7** the least (32.94 wt. %). Two compounds, **78** and **84**, decompose at temperatures below 200 °C (159 and 161 °C, respectively), indicating their low thermal stability and consequently lack of potential application in new energetic materials. Compound **72** shows the highest thermal stability (401 °C), followed by compounds **74** and **75** (375 and 343 °C, respectively). The table also shows that the lowest impact sensitivity was obtained for compounds **72**, **74** and **81** and the highest for compound **84** (5 J). As for friction sensitivity, compounds **72** and **81** are practically insensitive (values above 300 N). The lowest friction sensitivity values of 120 N were achieved by compounds **74** and **82**, as for RDX and HMX. Calculated values of detonation velocity are in the range of 7658 – 9571 m/s, the highest value was reached by compound **81**.

N1-substituted aminotriazoles

Literture indicates, that there are also energetic coordination compounds containing as a ligand triazoles, such as 1-amino-1,2,3-triazole (1-ATRI) and 1-amino-1,2,4-triazole.

There are various methods of synthesising this group of compounds. For example, the synthesis of 1-ATRI is the two-step amination reaction of 1,2,3-triazole. In the reaction, a mixture of isomers is produced, leading to obtaian isomerically pure product. In the first step of the synthesis, glyoxal and hydrazine hydrate are used. In the second step, freshly precipitated activated manganese dioxide, through its oxidation, has the ability to promote intramolecular cyclization of organic molecules [154]. The key intermediate bis-hydrazone can be prepared by condensing hydrazine hydrate and glyoxal. Another method of synthesis is using potassium triazolate treated with the amine reagent hydroxylamino sulfonic acid (HOSA) in water at 70 °C [155].

The figure below shows the synthesis route of energetic coordination compounds with 1-aminotriazole (Fig. 23).

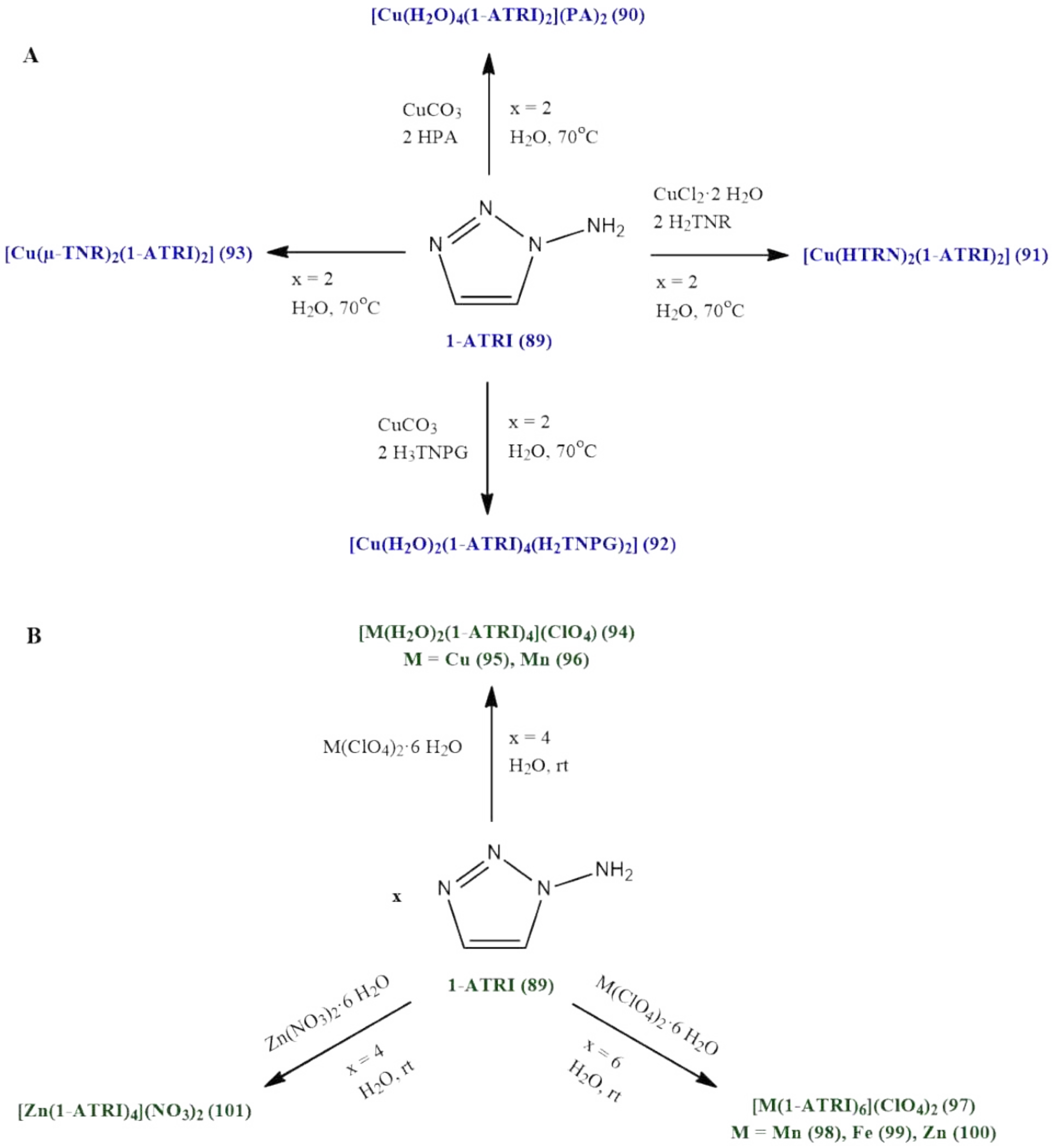


Figure 23: Scheme of synthesis: **A** - copper(II) 1-ATRI picrate **(90)**, 2,4,6-trinitro-3-hydroxyphenolate (HTNR) **(91)**, 2,4,6-trinitro-3,5-dihydroxyphenolate (H_2TNPG) **(92)**, and styphnate (TNR) **(93)** transition-metal(II) complexes; **B** - copper(II) **(95)**, manganese(II) **(96 and 98)**, iron(II) **(99)** and zinc(II) **(100 and 101)** 1-ATRI complexes. Based on [155]

The reaction shown on Fig. 23 of copper(II) salt with 1-ATRI and styphnic acid is highly pH dependent. As a result, a complex with a single or double deprotonated anion can be obtained. By using copper(II) chloride as the source of this metal, a complex is obtained in which the HTNR is responsible for the formation of closed octahedral coordination spheres. In contrast, by using copper(II) carbonate, complex with 1D-polymeric chains is obtained, due to the bridging styphnate [155]. The 1-ATRI perchlorate complexes may be anhydrous or contain two water ligands. The water-free complexes have comparable densities (Mn: 1.673 g/cm^3 (143 K); Fe: 1.697 g/cm^3 (123 K); Zn: 1,740 g/cm^3 (133 K)). These compounds also have high thermal stability in Fe(II), Cu(II), Zn(II) and Mn(II) ascending order. A similar trend could be observed for complexes with 1-methyl-5H-tetrazole and 1-amino-5H-tetrazole as ligands. The obtained compounds showed different responses to the laser ignition experiments, which can be correlated with their sensitivity. Some complexes can be described as insensitive (IS $>$ 40 J, FS $>$ 360 N) and others as extremely sensitive (FS $\leqslant$ 10 N). Selected complexes were also subjected to secondary explosive initiation tests. The result for two of them was positive, making them a potential alternative to lead based explosives. Compound **95** detonated in all of these tests, while **100** caused deflagration-to-detonation transition of PETN and **99** detonated during laser ignition tests. These results indicate the possibility of using these compounds as lead-free substitutes for initiating explosives (Tab. 12).

Table 12: Results of tests performed for selected complexes. Based on [155].

Compound	**T $_{\text{dec}}$ [°C]**	**IS [J]**[a]	**FS [N]**[b]	**ESD [J]**[c]	**HP**[d]	**HN**[e]	**LIT**[f]
90	188	$>$ 40	$>$ 360	1.22	-	-	dec.
91	177	1.5	80	0.04	-	-	dec.
92	153	2	160	0.30	-	-	dec.
93	194	3	60	0.05	-	-	dec.
94	167	1	0.45	0.10	def.	det.	det.
99	166	1.5	2	0.04	def.	def.	det.
100	188	3	6.75	0.07	def.	def.	-
101	188	6	45	0.70	def.	def.	-

[a] Impact sensitivity according to the BAM drop-hammer method
[b] Friction sensitivity according to the BAM friction tester
[c] Electroststic discharge sensitivity according to the ESD tester
[d] Hot plate test: def. - deflagration
[e] Hot needle test: def. - deflagration; det. - detonation
[f] Laser ignition test: dec. - decomposition; det. - detonation

The authors of the work [156] have obtained two energetic coordination compounds containing a ligand in the form of 4-amino-1,2,4-triazole (4-ATR) $[Cd(4\text{-}ATZ)_2(Ac)_2(H_2O)]$ (where Ac = acetate) and $[Cd(4\text{-}ATZ)_2(H_2O)_4](PA)_2$ (PA = picrate). In both cases, the coordination site in the triazole ring is at the position of the N1 atom. Compound containing Ac in the structure exhibit monoclinic crystal system, for PA-based compound there is a triclinic crystal system. The 4-ATR ligand is a versatile compound due to the alkaline nature of the compound, and can react with acids to form various EECs such as 4-amino-1,2,3-triazole perchlorate [157], a nitrate analogue [158] or 4-amino-1,2,4-triazole picrate of oxalic, succinic and adipic acids. 4-ATR can also act as a bidentate ligand, coordinating with a metal ion at the N1 and N2 atom positions in the triazole ring. Based on the authors' research [156], the study of thermal stability, the compound (4-ATR) $[Cd(4\text{-}ATZ)_2(Ac)_2(H_2O)]$, after gradual release of coordinated water from the molecule in the temperature range of 74.8 - 131.9 °C, loses its crystalline structure and then decomposes at 293 °C due to the breaking of coordination bonds. On the other hand, for $Cd(4\text{-}ATZ)_2(H_2O)_4](PA)_2$, two endothermic peaks can be observed on the thermogram, indicating a two-stage thermal decomposition (288.9 °C and 344.9 °C), in which the external PA anions are lost first. Considering the sensitivity parameters, the Ac anion-containing compound exhibits no sensitivity to impact and friction, unlike the PA anion-containing compound. For friction sensitivity, the firing rate (h_{50}) is 24 %, while impact sensitivity was estimated at 18.63 cm (hammer drop at a height of 150 cm).

There is also a coordination compound containing the zinc metal $[Zn(ATZ)_3](PA)_2 \cdot 2.5H_2O]_n$, in which there are three types of intramolecular hydrogen bonds [37]. The first between the carbon atom in the ATZ ligand and the oxygen in the PA molecule, the second between the carbon atom in the ATZ and the oxygen in the crystal water molecule and the third between the carbon atom and the oxygen in the two PA molecules. DSC analysis indicates that exothermic thermal decomposition occurs in three steps at temperatures of 276.3, 351.2 and 519.4 °C, respectively. Considering the sensitivity parameters, the compound shows no friction sensitivity, while the impact sensitivity is 27.8 J.

The literature also indicates energetic coordination compounds containing a copper ion, an azide anion and a ligand in the form of 3-nitro-1H-1,2,4-triazole (Hntz) - $[Cu(ntz)(N_3)(DMF)]_n$ and $[Cu(ntz)(N_3)(H_2O)]_n$ [159]. The introduction of an azide anion into the molecule and the functionalization of the triazole ring by introducing a nitro group can contribute to obtaining compounds with low sensitivity and high detonation performance. In addition to the high nitrogen content of 46.9 wt. % of the Hntz molecule, improvements in oxygen balance, they can provide a variety of possible coordination sites, which in turn allows finding stable compound structures. The authors of this study obtained both compounds by the one-pot hydrothermal method. The synthesis of the DMF-containing compound involved the preparation of an aqueous solution containing Htnz and N,N-dimethylformamide. Under continuous stirring at room temperature, NaN_3 was added after 30 minutes. The resulting mixture was then transferred to an autoclave for 3 days and stirred at 90 °C under autogenous pressure. The obtained crystals of the compound were washed with water and air-dried. The synthesis of the second compound proceeded in a similar manner, except that at first an aqueous solution consisting of $Cu(NO_3)_2 \cdot 3H_2O$, Hntz and NaN_3 was prepared. Based on structural analysis (X-ray diffraction study), both compounds were found to be isomorphic. $[Cu(ntz)(N_3)(DMF)]_n$ **(102)** has a monoclinic crystal system in which one metal cation (hexacoordinated by 4 nitrogen atoms and two oxygen atoms), one ligand and azide anion, and one coordinated dimethylformamide molecule are present. The difference in the structure of $[Cu(ntz)(N_3)(H_2O)]_n$ **(103)** is attribuable to the presence of one coordinated water molecule. Considering exothermic decomposition, the dimethyforamide-containing compound decomposes in two stages. In the first step, at 199.2 °C, the coordinated DMF molecules break off, followed by decomposition of the whole molecule at 279.5 °C. For the water-containing compound, a two-step decomposition also occurs, with the coordinated water breaking away at 108.8 °C, while the second step involves decomposition at 287.3 °C. The authors of this paper also determined the detonation parameters, whose calculated values are summarized in the following table (Tab. 13).

Table 13: Sensitivity and detonation parameters for ntz-based ECCs [159].

Compound	ρ **[g/cm^3]**	**IS [J]**	**FS [N]**	**P [GPa]**	**D [m/s]**[a]
102	1.748	> 40	> 360	23.42	7250
103	2.122	> 40	> 360	3.07	3260

[a] Calculated detonation velocity by EXPLO5

Tab. 13 shows that both compounds do not show sensitivity to impact and friction. The DMF-containing compound shows better detonation performance compared to the water-containing compound. Due to the release of coordinated water as a result of the exothermic decomposition of this compound, it had a significant effect on reducing the pressure and velocity of detonation. The table indicates that both compounds show no sensitivity to impact and friction. The compound containing DMF exhibits better detonation performance (detonation velocity above 7000 m/s) compared to the compound containing water (detonation velocity above 3000 m/s). The release of coordinated water as a result of the exothermic decomposition of this compound, significantly affected the pressure and speed of detonation. By introducing a solvent (DMF, H_2O) into the molecule, a higher heat of detonation can be achieved (1.81 kcal/g for the compound with DMF).

Another example of a compound being a 1,2,4-triazole derivative is 5-(4-nitro-1H-pyrazol-3-yl)-1H-1,2,4-triazol-3-amine (NPTA) and (Z)-N-(5-(4-nitro-1H-pyrazol-3-yl)-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)nitramide (NPTN) [160]. The synthesis scheme of the ligands is shown in the figure below (Fig. 24) [161]. These ligands consist of a pyrazole molecule and a triazole molecule, which are linked together by a carbon-carbon bond.

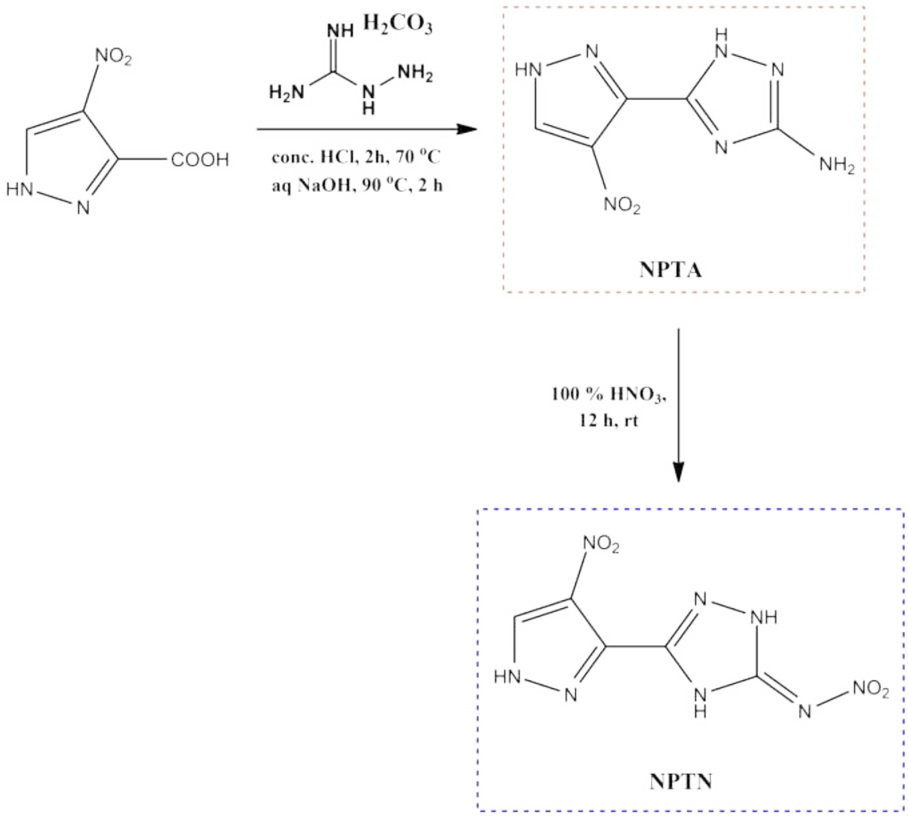


Figure 24: Synthesis scheme of NPTA and NPTN ligands.

The authors of the work [160] obtained and characterised a series of eneregtic coordination compounds containing NPTA or NPTN ligand with metals such as Ni, Co and Zn. Compounds contain NPTN ligand include respectively: $[M(NPTA)(H_2O)_3]_2 \cdot 2NO_3$ (where M = Ni **(104)**, Co **(105)**, Zn **(3)**) and $[M(NPTN)(H_2O)_3]_2$ (where M = Ni **(107)**, Co **(108)**, Zn **(109)**). The synthesis of ECCs involved mixing the ligand and the corresponding metal nitrate in a mixture of methanol-water solvents in an equimolar ratio. The resulting compounds were then filtered by gravity and allowed to evaporate residual solvent. Considering the crystal structure, Ni(II), Co(II) and Zn(II) ions are hexacoordinated to form an octahedral structure. In addition, all compounds are dimeric in nature. Compounds **(104)** and **(106)** exhibit a monoclinic crystal system, compound (105) a triclinic system. Compounds containing the NPTN ligand **107** – **109** are characterised by a triclinic crystal system. Due to the presence of numerous hydrogen bonds, such as between the amine group and the oxygen in the nitrate anion, or the oxygen in the coordinated water molecule and the oxygen in the nitrate anion, these compounds can form stable energetic structures. The authors of the paper also determined the energetic properties, which were shown in Tab. 14.

Table 14: Sensitivity and detonation parameters for ECCs containing NPTA and NPTN ligands.

Compound	ρ **[g/cm^3]**	**T$_{dec.}$ [°C]**	**IS [J]**	**FS [N]**	**P [GPa]**	**D [m/s]^a**
104	1.99	129	> 40	> 360	20.34	7147
105	1.95	331	> 40	> 360	15.94	6653
106	1.98	352	> 40	> 360	15.71	6818
107	1.94	216	> 40	> 360	23.29	7241
108	2.06	349	> 40	> 360	26.34	7522
109	2.05	318	> 40	> 360	24.80	7512

All of the compounds exhibit high density, taking values from 1.94 to 2.06 g/cm^3. In addition to being thermally stable (exothermic decomposition in the range of 216 – 352 °C, with the exception of compound (Zn)), they do not show sensitivity to impact and friction, which is advantageous in terms of their further use, obtaining materials that are safe to handle. Considering pressure and detonation velocity, compounds containing the NPTN ligand reach the highest values (detonation velocity in the range from 7241 to 7522 m/s).

As a 1,2,4-triazole derivatives, there is also compound such as 3,4-diamino-1,2,4-triazole or 3,5-diamino-1,2,4-triazole (DATr), which contain high nitrogen content of 70.67 wt. % [162,163]. Due to the presence of two amine groups, in which nitrogen atoms posses free electron pairs, coordination with central metal ions is possible. Moreover, the presence of intermolecular and intramolecular hydrogen bonds affects to ensure higher stability of the molecule [164]. Intermolecular bonds occur between coordinated water molecules, oxygen atoms derived from nitrate anions, or crystal water molecules and amino groups of DATr ligand molecules. Intramolecular hydrogen bonds, meanwhile, occur between oxygen atoms in crystalline water and also nitrogen atoms included in the triazole ring. In addition, because the triazole ring of DATr has different coordination sites, it can have the character of a monodentate or bidentate ligand. Hence, the advantage of its application is the possibility of creating new compounds with different structures.

The authors of the work [163] obtained a series of energetic coordination compounds incorporating the DATr ligand and metal nitrates of Mn(II) **(110)**, Co(II) **(111)**, Ni(II) **(112)** and Zn(II) **(113)**. The synthesis of the compounds involved the addition of nitric acid to an aqueous solution of silver carbonate. The resulting reaction mixture was introduced into an aqueous solution containing DATr and hydrochloric acid and then stirred. After the precipitation of crystals, the precipitate was filtered and leveled to neutral pH. In the next step, the corresponding metal nitrate $M(NO_3)_2$ was introduced. A suspension was obtained, which was then filtered. Based on the crystallographic data, it was indicated that all compounds except the Mn-containing compound exhibit a monoclinic crystal system. Moreover, in these compounds, the DATr ligand exhibits bridging modes linking two metal ions. Considering thermal stability, the compounds obtained by the authors of this paper decompose at temperatures above 260 °C, indicating their high thermal stability. The thermograms show peaks from both endothermic and exothermic decomposition. This is associated with several stages of decomposition. First, the water molecule is lost, then there is a phase transformation and decomposition of the whole molecule. Impact and friction sensitivity tests were also performed. The results of impact sensitivity are given for a 50 % probability of sample explosion (h_{50}), from which it can be seen that compound **(110)** and **(113)** are not sensitive to impact, while for **(110)** and textbf(112) h_{50} is 21.35 and 48.36 cm, respectively. The results of friction sensitivity were determined by the firing rate at an angle of 90° in the direction of friction. They show that compound **(112)** and **(113)** do not show sensitivity for friction, while for **(110)** and **(111)** the value is 28.35 and 19.34 cm, respectively. Due to their relatively low sensitivity to friction and impact, they are considered to be safe for use.

By changing the anion to perchlorate, authors of the paper [162] obtained ECCs with metal: Mn **(59)**, Co **(60)**, Ni **(61)** and Zn **(62)**. The synthesis of the compounds involved the introduction of a corresponding aqueous solution of metal chlorate into an aqueous solution containing DATr and hydrochloric acid. Due to the neutralization of the acidic nature of DATr, LiOH was previously introduced into the solution. The reaction was carried out at 60 °C, and after completion, the resulting precipitate was filtered and dried. Based on crystallographic data, compound **(60)** was found to exhibit a rhombohedral crystalline system, compound **(61)** a trigonal system and compound **(62)** a triclinic system.

These compounds exhibit similar properties to their nitrate analogueous, i.e. high thermal stability, but they are more sensitive to mechanical stimuli, what is the characteristic of compounds containing perchlorate anion. Most of them are sensitive to friction, but these values are still lower than those of lead(II) azide. The following table (Tab. 15) summarizes selected physicochemical and energetic parameters of chlorate analogues.

Table 15: Properties of DATr-based nitrate and perchlorate complexes [162].

Compound	T $_{\text{dec.}}$ [°C]	E_a [kJ/mol][a]	Q_V [MJ/kg][b]	IS [J]	FS [N]
114	347.7	101.65	8.91	> 40	128
115	328.6	112.8	9.51	1.8	84
116	361.9	183	8.73	2.7	60
117	350.9	175.9	8.24	> 40	216

[a] Activation energy

[b] Constant volume energy of combustion

Chlorate analogues have high thermal stability (over 300 °C). The most thermally stable is the compound containing the Ni(II) ion, which decomposes at 361.9 °C. According to the literature, stable ECCs that decompose at temperatures above 200 °C are assumed to meet the criterion for "green" explosives and can be potentially used for further research [165].

Tetrazoles and its derivatives

Tetrazoles are compounds with five ring members containing one carbon atom and four nitrogen atoms. There are three isomers of unsubstituted 1,2,3,4-1H-tetrazole: 1H-, 2H- and 5H-tetrazole, which differ in the position of the double bonds (Figure 25).

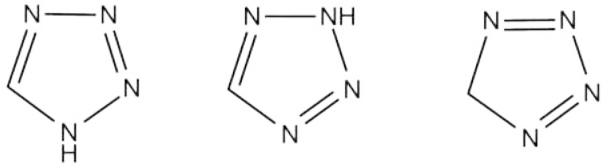


Figure 25: Isomers of unsubstitued tetrazole compounds.

The tetrazole molecule has 79.98 wt. % nitrogen in its structure. As with triazole compounds, it is possible to attach different substituents to the ring as for example nitro, nitrate or nitramine groups [166]. Compounds such as 1-H-tetrazolium and its derivatives can be used as nucleophiles to integrate the tetrazolium ring into other molecules. The combustion products of tetrazolium-based energetic are environmentaly friendly, containing mainly water, carbon dioxide and nitrogen. The figure below (Fig. 26) show an examples of substitued tetrazole ligands and their derivatives. These compounds **(121 - 129)** were arranged according to the increasing amount of nitrogen in the molecule, respectively: 60.87; 66.63; 66.64; 70.71; 73.67; 78.38; 79.98; 82.33; 83.97 wt. %.

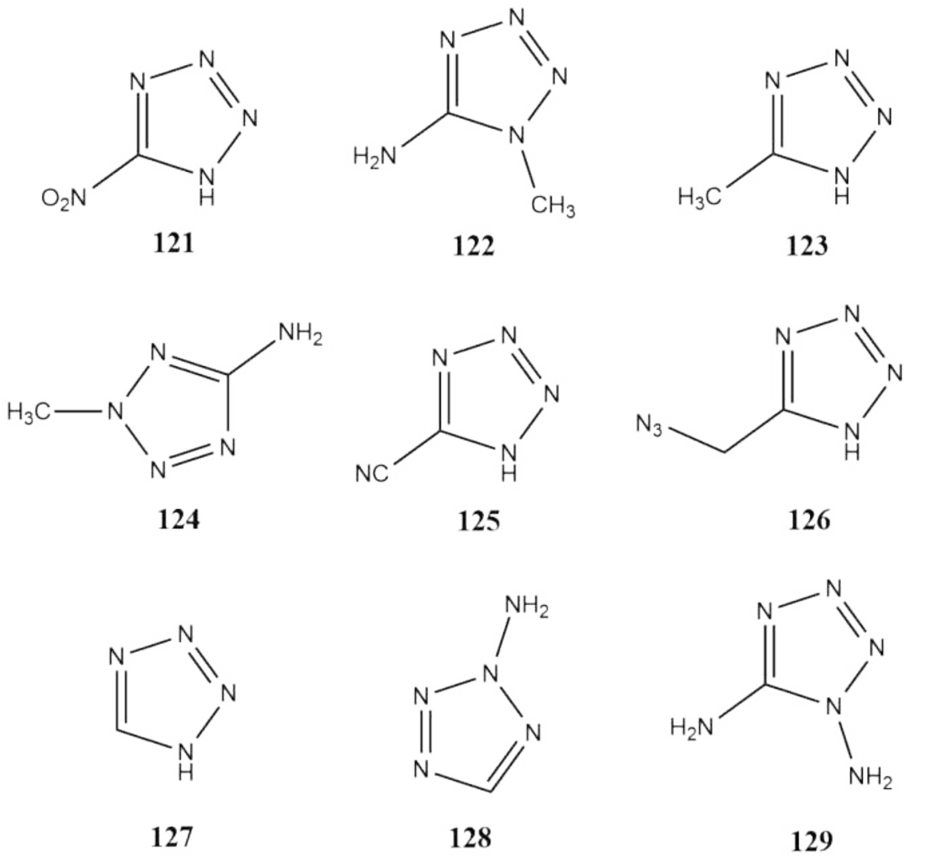


Figure 26: Examples of tetrazole ligands and its derivatives.

An example of the ECCs containg tetrazole ligands BNCP **(130)**, refered as bis-(5-nitro-2H-tetrazolato-N^2)tetraammine cobalt(III) perchlorate [167]. BNCP gained notoriety in the 1990s as part of a project to create substitutes for primary lead-based explosives. This compound contains perchlorate anion, which makes it less attractive for the point of view of "green" chemistry, but compared to lead azide, this compound is still less harmful to the environment [168]. The synthesis of BNCP is carried out in several steps. First, a solution of 5-aminotetrazole and copper sulfate pentahydrate is prepared, containing nitric acid, which is then slowly introduced into sodium nitrite after cooling (5 °C). The resulting solution is stirred at a temperature not exceeding 18 °C. The precipitated product is filtered under reduced pressure, and then washed with nitric acid and water successively. The resulting product is a salt of cupric acid, into which water is introduced, followed by a solution of sodium hydroxide until it reaches pH 9. The resulting suspension is heated to a temperature equal to 80 °C, at which copper oxide precipitates. After it is filtered out, the filtrate is cooled to ambient temperature, then a solution of nitric acid is added to obtain pH 4. The liquid obtained as a result of the reaction, is used in further steps to obtain coordination compounds based on BNCP. The authors of the paper [167] also obtained bis-(5-nitro-2H-tetrazolato-N^2)tetraammine nickel(III) perchlorate refered as BNNP **(131)**, mono-(5-nitro-H-tetrazolato-N)triammine copper(II) perchlorate refered as MNCuP **(132)** and also mono-(5-nitro-H-tetrazolato-N)triammine zinc(II) perchlorate referd as MNZnP **(133)**. Some properties of BNCP and its analogues conatining nickel(II), copper(II) and zinc(II) ion were shown in table below (Tab. 16).

Table 16: Properties of energetic coordination compounds containing BNCP and its analogues.

Compound	**Metal content [%]**	**bulk density [g/cm^3]**	**T$_{dec}$[°C]**	**IS [J]**[a]	**FS [N]**
130	12.90 (Co)	0.30-0.60	268	32	3
131	12.87 (Ni)	0.54	278	30	3
132	19.40 (Cu)	0.65	260	30	4.8
133	19.65 (Zn)	0.85	120	36	14

[a] Recalculated based on experimental data, energy corresponding to 50 % initiation chance

Considering thermal stability, it can be seen that the most stable is the **(131)** compound, whose decomposition occurs at 268 °C, while the lowest decomposition temperature of 120 °C corresponded to the analogue containing Zn(II) ion. The results of sensitivity tests (impact, friction) indicate that they exhibit a weaker response to mechanical stimuli than traditional primary explosives.

In turn, the authors of the paper [169] obtained a series of energetic coordination compounds containing a ligand in the form of 1-methyl-5H-tetrazoles (MTZ) with metal ions Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I) and anions in the form of chloride, nitrate, perchlorate, cyanodinitromethane, picrate and styphnate. MTZ ligand **(123)** contains 66.63 wt. % nitrogen. As a ligand, is neutral and does not have an acidic proton, so it can form as well as cationic coordination compounds containing many oxidizing anions. In addition to its application in the synthesis of ECCs it may be used in pyrotechnic [170] and propellant compositions [171].

MTZ may be synthesised in several ways. One way is a cycloaddition reaction using sodium azide, triethyl orthoformate and methylamine in acetic acid [172]. Another way is the nucleophilic methylation reaction of 1H-tetrazolium using methyl iodide, the scheme for the synthesis of MTZ of which is shown in the figure below (Fig. 27). However, the reaction yields a mixture of products consisting of 1-methyl-5H-tetrazolium and 2-methyl-5H-tetrazolium [173], but it is possible to isolate a single product from the mixture using, for example, by column chromatography [167].

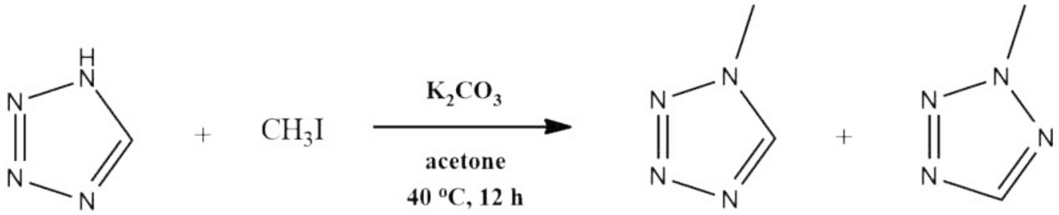


Figure 27: Synthesis scheme of 1-methyl-5H-tetrazole.

The following figure (Fig. 28) presents a simplified scheme for the synthesis of ECCs containing the MTZ ligand and the aforementioned metals and nitrate and perchlorate anion. The synthesis of ECCs involved combining solutions of MTZ with a divalent metal salt at the appropriate molar ratio at room temperature. In the synthesis of the majority of compounds, the authors of the paper, decided to choose water as the reaction medium, considering its lack of toxicity, its very low price and its exhibiting very good solubility for metal salts and tetrazolium derivative. For the synthesis of compounds containing perchlorate anion, water-containing reagents were not introduced. By varying the amount of added ligand, it is possible to obtain compounds with different structures, i.e. all ligands can be bound to metal ions (compounds 15-20), or by using an excess of ligand, it is possible to obtain coordination compounds with two additional co-crystallized tetrazoles (21-26).

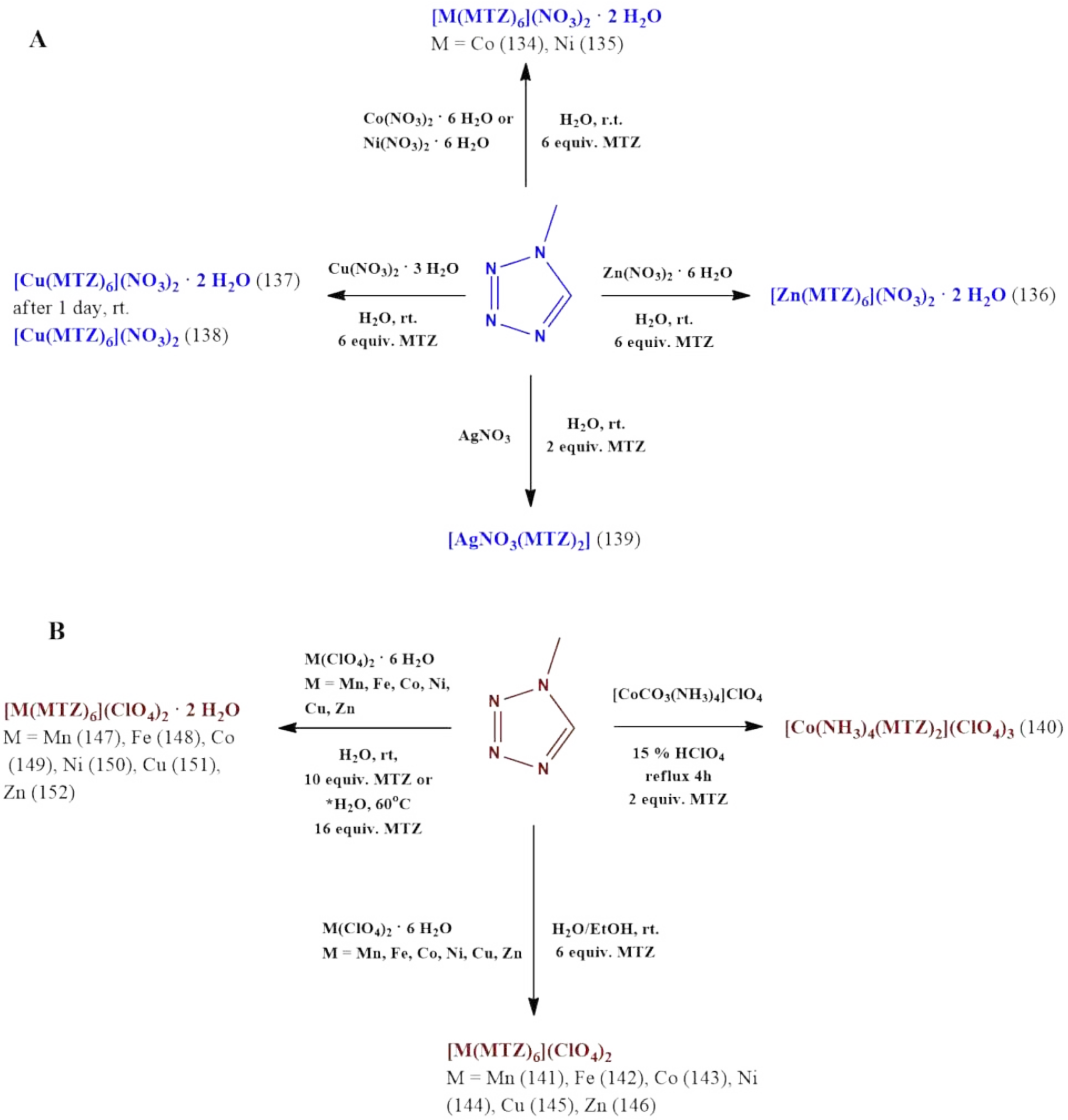


Figure 28: Synthesis scheme of ECCs based on 1-methyl-5H-tetrazole, metal nitrate (A) and metan perchlorate (B).

The following table shows selected properties of the described compounds (Tab. 17).

Table 17: Properties of ECCs based on 1-methyl-5H-tetrazole, metal nitrate and metan perchlorate.

Compound	T $_{\text{dec.}}$ [°C]	IS [J]	FS [N]	ESD [J]
MTZ	206	> 40	> 360	1.50
134	199	> 40	> 360	1.50
135	194	> 40	324	1.50
136	196	> 40	> 360	0.40
138	160	> 40	> 360	1.50
139	119	40	160	0.15
140	201	9	160	0.036
141	223	7	120	0.08
142	213	1	60	0.10
143	253	3	60	0.50
144	271	5	60	0.10
145	211	2.5	54	0.08
146	221	20	120	0.25
147	211	7	216	0.46
148	215	10	120	0.40
149	210	10	80	0.13
150	207	6	192	0.20
151	206	7	72	0.20
152	212	10	144	0.60

For most compounds, the temperature of exothermic decomposition oscillates at 200 °C. The highest value was registered for compound 144 (271 °C. For compounds containing water in the structure, the occurrence of a peak for endothermic decomposition is characteristic, indicating the loss of a water molecule. For compounds containing perchlorates, an increase in thermal stability relative to the metal used was observed in the following order: Cu < Fe < Zn < Mn < Co < Ni. Based on impact and friction sensitivity values, it can be concluded that MTZ is a compound insensitive to mechanical stimuli. The introduction of other previously mentioned oxidising anions such as picrate, styphate causes an increase in impact and friction sensitivity (impact: 2-40 J, friction: 160-360 N, ESD: 0.13-1.50 J).

Another examples of a ligand used to synthesise ECCs are 1-amino-5H-tetrazole (1-AT) and 2-amino-5H-tetrazole (2-AT) **(128)** [174]. Compared to the MTZ ligand, the replacement of the methyl group in the molecule with an amino group (the presence of an additional N−N single bond) increased the nitrogen content of the molecule to 82.33 wt. %. The authors of the paper [174] obtained a series of ECCs containing ligand 1-AT, alternating 2-AT with metal ions Mn(II), Fe(II), Cu(II), Zn(II) and anion in the form of Cl^-, NO_3^-, ClO_3^-, ClO_4^-. The figure below shows a two synthesis route of 1-AT and 2-AT (Fig. 29).

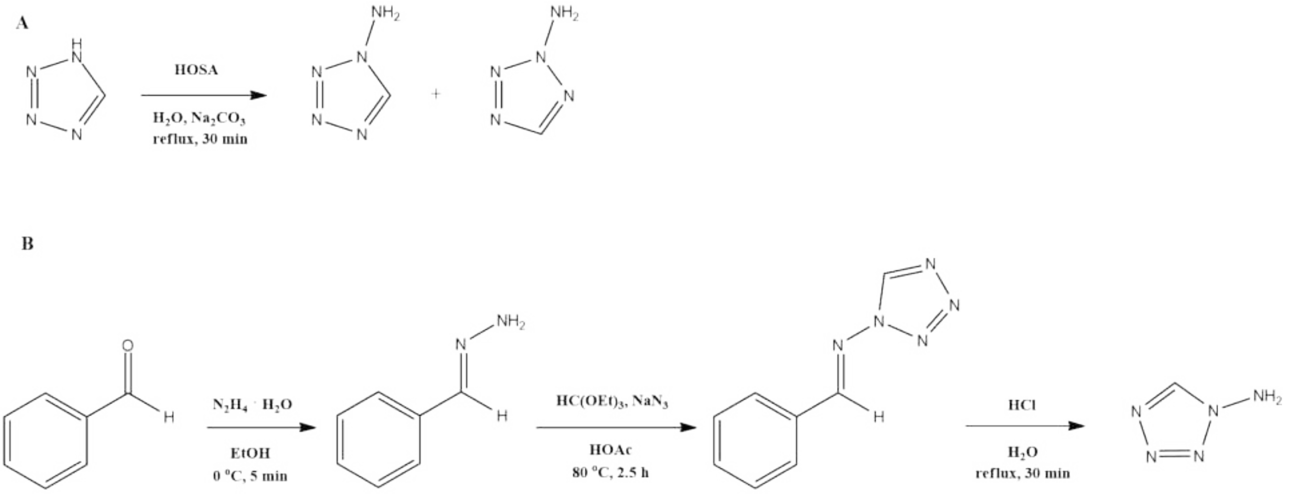


Figure 29: Two way synthesis of 1-AT and 2-AT through amination reaction using hydroxylamine-O-sulfonic acid (HOSA) (A) and by three-step reaction using benzaldehyde.

The synthesis of 1-AT can take two approaches. The first method involves direct amination of the 1,5H-tetrazole molecule with HOSA, a reaction that produces two isomers of tetrazole containing an amino group. This reaction follows the mechanism of a nucleophilic substitution reaction [175]. The resulting isomers can be separated on a flash type chromatography column on silica gel using a solvent mixture of EtOAc/DCM in a molar ratio of 5:1. The second method of synthesis is carried out in three steps. In the first step, benzaldehyde is condensed with hydrazine hydrate at a lower temperature (0 °C) to prevent the formation of bisbenzhydrazone. In the second step, the reaction proceeds with the cyclization of benzhydrazone with triethyl orthoformate and sodium azide, resulting in the closure of the benzhydrazone ring containing the free amino group. In the final step, as a result of the use of hydrochloric acid, the benzyl group is cleaved off, while the benzaldehyde is removed by evaporation under reduced pressure. The synthesis of energetic coordination compounds involved introducing an aqueous solution of a metal salt into an aqueous solution of a ligand at room temperature.The synthesis scheme for selected ECCs containing 1-AT and 2-AT is shown below (Fig. 30).

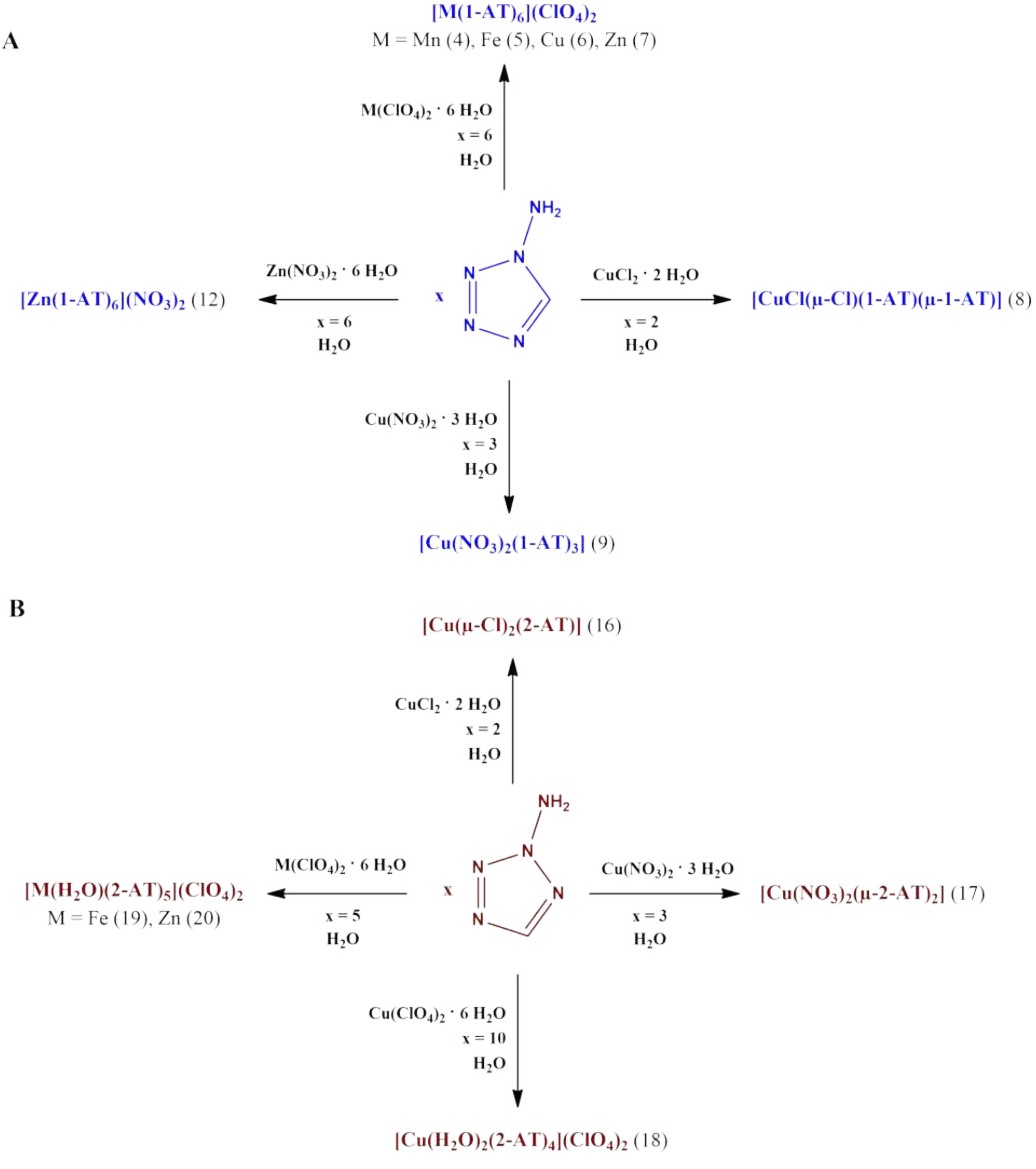


Figure 30: Synthesis scheme of ECCs containing 1-amino-5H-tetrazole (A) and 2-amino-5H-tetrazole (2) [174].

An essential influence on the structure of the resulting compound is the use of an appropriate molar ratio of ligand to metal salts. For example, in the case of the synthesis of compound 18, not using an excess of ligand can lead to obtaining a hexacoordinated tetrazolium complex as a by-product that undergoes spontaneous decomposition. In this case, the use of an excess of ligand twice as much, compared to compounds 19 and 20, results in a compound containing an additional water molecule and cocrystallized aminotetrazole. In order to evaluate the applicability of the above compounds as initiating explosives, the following table presents the parameters of sensitivity to friction, impact, sensitivity to electrostatic discharge and also the results of hot needle and hot plate tests (Tab. 18).

Table 18: Results of tests performed for 1-AT and 2-AT-based coordination compounds.

Compound	**T $_{dec.}$ [°C]**	**IS [J]**	**FS [N]**	**ESD [mJ]**	**HP[a]**	**HN[b]**
1-AT	182	< 1	64	-	-	-
2-AT	197	< 1	36	-	-	-
153	195	< 1	0.5	11	det.	def.
154	187	< 1	< 0.1	12	det.	det.
155	174	< 1	< 0.1	5	det.	det.
156	188	< 1	0.5	12	def.	det.
157	175	3	60	50	-	-
158	161	3	2.25	10	-	-
159	180	< 1	6	620	def.	def
160	171	< 2	40	10	-	-
161	157	< 1	2	10	def.	def.
162	173	1	0.4	10	det.	det.
163	159	1.5	0.15	10	det.	det.
164	200	1.5	0.5	10	det.	det.

[a] Hot plate test: def. - deflagration, det. - detonation
[b] Hot needle test: def. - deflagration; det. - detonation

Considering thermal stability, almost all compounds decompose exothermically at around 200 °C, with the exception of compound **(158)**, **(161)** and **(161)** (at 161, 157 and 159 °C, respectively), indicating their relatively good thermal stability. In addition, all compounds show high sensitivity to impact (values ranging from 3 to less than 1 J), friction (values ranging from 60 to less than 1 N) and static electricity (620 to 5 mJ), as for the 1-AT and 2-AT ligands themselves. It can be seen that iron-containing and copper-containing compounds are the most sensitive to mechanical stimuli. Hot plate and hot needle tests, on the other hand, made it possible to determine whether a compound deflagrates or detonates. On this basis, compounds were selected for which the initiating ability was tested against pentaerythritol tetranitrate (PETN) in electric detonators. The test setup consisted of a copper detonator, which included a coordination compound as an initiating explosive in the amount of 50 mg and a secondary explosive (PETN) in the amount of 200 mg. Based on the tests, it was found that coordination compounds containing perchlorate anion were not able to fully initiate PETN (**(158)** and **(161)**), while compounds containing nitrate anion **(153)**, **(156)** and **(164)** gave a positive result. For these reason, they may be considered as alternatives for lead-free initiation materials.

The literature indicates that there are also energetic coordination compounds containing a ligand in the form of 1-ethyl-5H-tetrazole (1-ETZ), 1-azidoethyl-5H-tetrazole (AET) with nitrate anion, perchlorate anion and metals such as Cu(II), Fe(II), Zn(II) and Ag(I) [176]. Both ligands do not contain acidic protons and can therefore be incorporated into neutral coordination compounds containing anion such as nitrates, perchlorates, picrates, styphnates or 2,4,6-trinitro-3,5-dihydroxyphenolates (H_2TNPG). Depending on the changes in the reaction conditions for ECCs, i.e. solvent (ethanol, water), temperature (room or elevated temperature), metal salts (hydrated or non-hydrated salts) it is possible to obtain different compounds, what was shown in the Fig. 31.

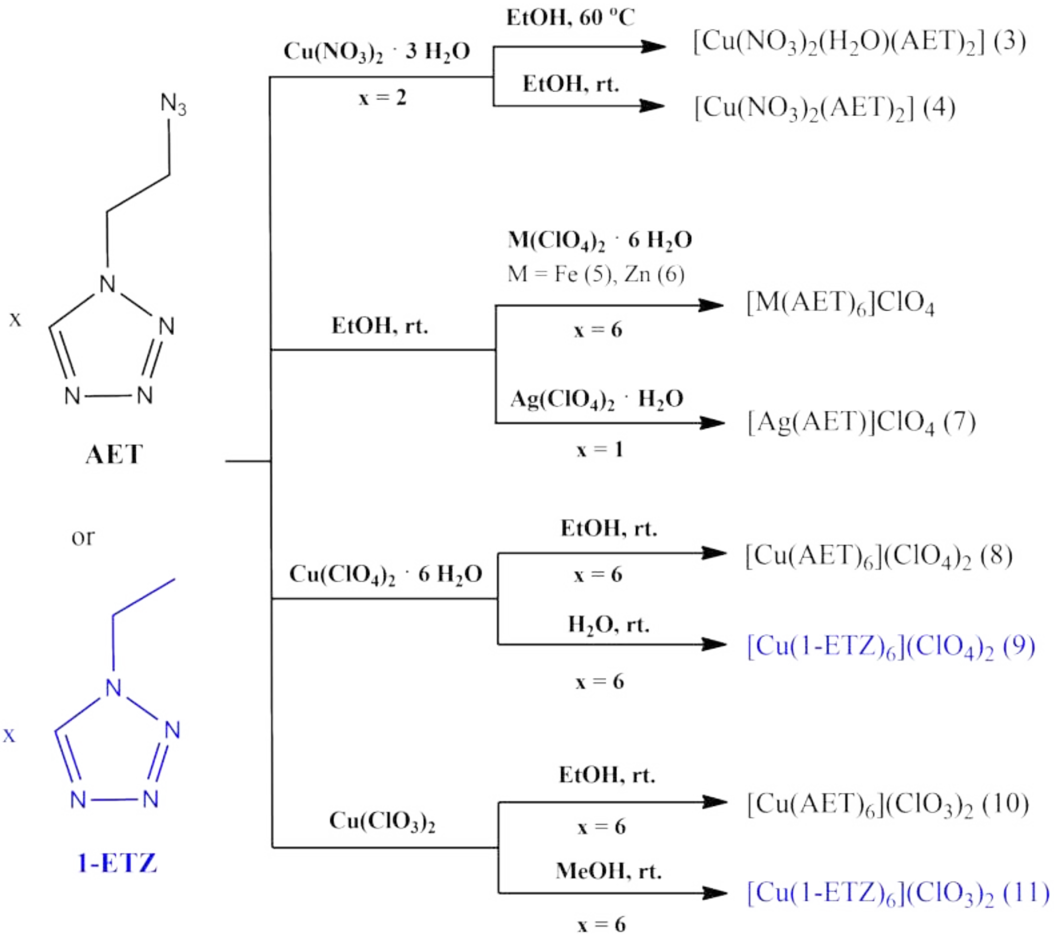


Figure 31: Synthesis scheme of ECCs containing 1-azidoethyl-5H-tetrazole and 1-ethyl-5H-tetrazole [176].

The authors of the work determined the geometry of the majority of the obtained compounds. Compounds containing a perchlorate anion have octahedral coordination spheres. Coordination of the 1-ETZ ligand and AET with the metal is carried out by nitrogen atoms located in the tetrazole ring, the only exception is compound **(169)**. The coordination sphere for compounds **(166)**, **(167)** is monoclinic, for **(165)**, **(169)** and **(171)** triclinic, whereas for compound 11 trigonal. The authors of this paper also determined the thermal stability, sensitivity parameters of the obtained compounds (except for compound **(166)**) and performed a hot plate and hot needle test. The results are shown in the following table (Tab. 19).

Table 19: Results of tests performed for AET and 1-ETZ-based coordination compounds.

Compound	**T $_{dec.}$ [°C]**	**IS [J]**	**FS [N]**	**ESD [mJ]**	**HP**[a]	**HN**[b]
AET	193	9	> 360	-	-	-
1-ETZ	208	> 40	> 360	-	-	-
3	152	10	108	840	def.	def.
5	151	3	3.75	65	det.	det.
6	196	15	40	368	def.	def.
7	165	< 1	0.6	65	det.	det.
8	158	< 1	15	368	def.	det.
9	210	10	120	960	def.	def.
10	146	2.5	4	226	def.	det.
11	158	7	60	608	def.	def.

[a] Hot plate test: def. - deflagration, det. - detonation
[b] Hot needle test: def. - deflagration; det. - detonation

The obtained compounds do not show high thermal stability - exothermic decomposition occurs at about 150 °C, except for ligand 1-ETZ (208 °C) and compound 6 and 9 (196 and 210 °C, respectively). Thermograms indicated that only compound 3 showed two signals originating from endothermic decomposition. The first at 94 °C, indicating melting of the compound, and the next at 121 °C, indicating loss of the coordinated water molecule. Thermograms of samples 6 and 8-11 display a single endothermic peak indicating only melting of the sample.

The results of sensitivity to impact and friction are highly variable, but compounds with AET as ligand are more sensitive than compounds based on 1-ETZ. However, from the compounds discussed, only compound 2 (1-ETZ) can be considered completely insensitive to mechanical stimuli. Ligand AET also exhibits no friction sensitivity, in contrast, it can be considered sensitive to impact (9 J). Compared to other compounds, compound 6 (containing Zn ion) can be considered the least sensitive. The greatest sensitivity to impact and friction is observed in compounds 5, 7 and 8, which are recognized as highly sensitive or extremely sensitive. On this basis, it can be concluded that compounds containing 1-ethyl-5H-tetrazoles can be classified as secondary explosives, and the others as initiating materials. On the other hand, on the basis of the HP and HN test, two compounds capable of fully initiating PETN were selected

- 5 and 7. The rest underwent deflagration, which is not favorable for their potential use in exchange for lead(II) azide.

Compound [Ag(AET)](ClO_4) punctured a copper witness plate, making it one of the rare examples of silver complexes capable of PENT initiation. The iron(II) perchlorate complex also showed positive results in these tests. This compound also detonated during laser ignition test between energies ranging from 25.5 mJ to 30 mJ. The rest of the complexes also showed responses to laser irradiation. AET is a more energetic ligand compared to 1-ETZ. Complexes with this ligand are classified as primary explosives, while with unsubstituted 1-ETZ are classified as secondary explosives.

Another compound that can be used as a ligand is 2,2-bis(5-tetrazolyl)propane (5-DTP) [177]. This compound is obtained by the cycloaddition reaction of dimethylmalonononitrile and sodium azide. The catalyst for the reaction is zinc(II) bromide partially dissolved in water. Propan-2-ol is also introduced into the reaction mixture. In the next step of the reaction, the mixture is refluxed at 110 °C for 24h. After the reaction is completed, hydrochloric acid is introduced to dissolve the precipitate, followed by extraction with ethyl acetate. The resulting product is recrystallized with water. The authors of this work obtained a series of energetic coordination compounds containing ligand in form of 5-DTP, metal salts of Cu(II), Co(II), Ni(II) and Zn(II) and anion of ClO_4^-, NO_3^-, SO_4^{2-}, Cl^-. The synthesis of ECCs involved mixing aqueous solutions of the salts with the ligand in an acidic medium as the reaction medium at elevated temperature (80 °C). The use of dilute acid as a solvent in the recation gives the possibility of obtaining complex compounds of cationic or neutral nature with a non-oxidizing anion, such as chlorides, or with an oxidizing anion, such as perchlorate anion (Figure 32.

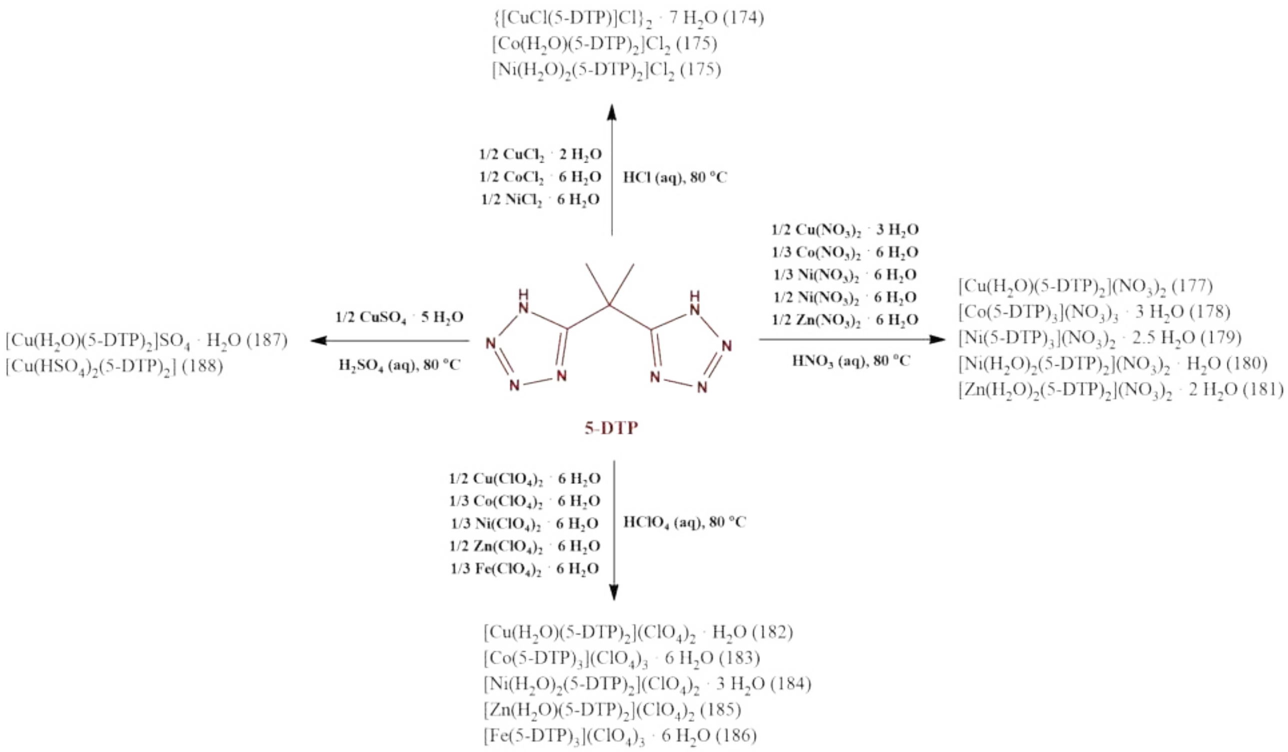


Figure 32: Synthesis scheme of ECCs containing 2,2-bis(5-tetrazolyl)propane [177].

Most of the compounds obtained exhibited a monoclinic crystal system and a triclinic system for compounds **(181)** and **(188)**. Due to the disordered structure of compounds **(178)**, **(179)**, **(183)**, **(184)** and **(186)**, it was not possible to determine their crystal structure. Due to the disordered structure of compounds **(178)**, **(179)**, **(183)**, **(184)** and **(186)**, it was not possible to determine their crystal structure. With the exception of compound **(188)**, thermal stability, sensitivity to friction, impact, electrostatic discharge and also hot plate and hot needle test were determined for selected compounds. The results of the tests are summarized in the following table (Tab. 20).

Table 20: Results of tests performed for 5-DTP-based coordination compounds.

Compound	**$T_{\text{dec.}}$ [°C]**	**IS [J]**	**FS [N]**	**ESD [J]**
5-DTP	235	30	> 360	1.50
174	259	> 40	> 360	1.50
174	253	> 40	> 360	1.50
176	207	> 40	> 360	1.50
177	293	8	> 360	1.50
178	267	10	> 360	1.50
179	203	5	324	1.50
180	163	10	360	0.15
181	170	40	> 360	0.20
181	251	3	10	0.065
183	206	12.5	72	0.50
184	190	12	216	0.75
185	256	2	20	0.20
186	176	< 1	15	0.10
187	225	> 40	> 360	0.75

Most of the compounds show high thermal stability - exothermic decomposition occurs at temperatures above 200 °C, reaching as high as 293 °C for compound **(177)**. Less stable are compounds **(180)**, **(181)**, **(184)** and **(186)**, whose exothermic decomposition temperatures reach 163, 170, 190 and 176 °C, respectively. With regard to sensitivity to impact, friction and electrostatic discharge, ligand 5-DTP can be regarded as an insensitive compound. Similarly, the same is the case with chloride-containing compounds **(174-176)**. Replacing the chloride with a nitrate group (compounds **(177-181)**) results in an increase in impact sensitivity reaching values in the range of 5 to 10 J and partially increasing electrostatic discharge sensitivity up to 0.15 J for compound textbf(180). Changing the anion from nitrate to perchlorate (compounds **(182-186)**) results in a further decrease in sensitivity values. For impact sensitivity, the range is from < 1 to 12.5 J, friction 10 to 72 N and for electrostatic discharge sensitivity in the range of 0.065 to 0.50 J. Of the compounds obtained, compounds 10 and 13, for which hot plate and hot needle tests were carried out, were selected as the most promising for further use as potential replacements for lead-based materials. As a result of the test, it turned out that both compounds did not undergo detonation process only deflagration process, which in this context is an undesirable process.

The literature indicates that tetrazole rings are also the building block unit for metal-organic frameworks (MOFs) [178]. The authors of the paper [179] obtained energetic MOFs compounds containing ligand in the form of 5-methyltetrazole (mtz) and 5-aminotetrazole (atz) with metal ions Mn(II), Cu(II): $[Mn_5(mtz)_{6.1}(atz)_{2.9}(NO_3)]$ (eMOF-1) and $[Cu(mtz)_2]$ (e-MOF-2). Synthesis of eMOF-1 involved mixing the two ligands in a 1:1 molar ratio with an aqueous solution of manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$ in a solution of N,N-dimethylformamide (solvothermal reaction, carried out at 120 °C). The synthesis of eMOF-2, meanwhile, involved mixing an aqueous solution of copper nitrate $[Cu(NO_3)_2]_2 \cdot 5H_2O$ with an aqueous solution of mtz ligand (hydrothermal synthesis, carried out at 85 °C). Based on DSC analysis, both compounds were found to be highly thermally stable, their exothermic decomposition occurring at 387 and 368 °C, respectively. Impact and friction sensitivity tests found both compounds to be insensitive (IS $>$ 40 N, FS $>$ 360 N). Detonation parameters were also determined. The compound eMOF-1 achieves at a density of 1.914 g/cm^3 a detonation pressure of 26.16 GPa and a detonation velocity of 7551 m/s, while eMOF-2 achieves at a density of 1.742 g/cm^3 a detonation pressure of 11.6 GPa and a detonation velocity of 5153 m/s. It can be noted that the detonation parameters of eMOF-1 are close to those for RDX or HMX, indicating that the compound can be classified as a secondary explosive. As mentioned earlier, reaching higher detonation parameters may depend on the nitrogen content of the molecule. The eMOF-1 compound has 51.05 wt. % nitrogen, while eMOF-2 has 48.78 wt. %, which would explain the achievement of lower detonation pressure and velocity.

The literature also contains information indicating the possibility of functionalizing the 5-aminotetrazole molecule, 4-amino-3,5-dinitropyrazole (ADNP), which causes an increase in density, thereby providing better detonation parameters (pressure, detonation velocity) of target compounds [180]. The introduction of ADNPs into 5-aminotetrazole makes it possible to obtain new ligands, methylene-linked molecules, referred to as DMPT-1 and DMPT-2 [181]. The synthesis involves the reaction of 1-(chloromethyl)-3,5-dinitro-1H-pyrazole-4-amine (CDPA) with 5-aminotetrazole in KOH and KI medium. The reaction produces a mixture of two isomers. Depending on the temperature at which the reaction is carried out, 80 or 60 °C, the amount of a given isomer in the reaction mixture changes, as shown in the figure below (Fig. 33).

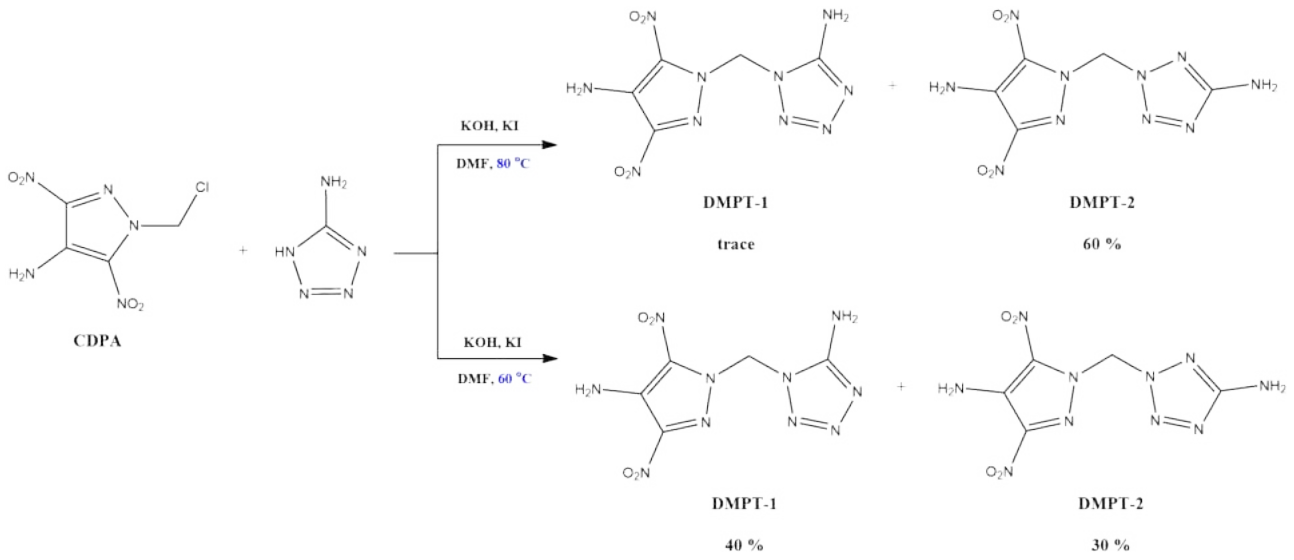


Figure 33: Synthesis scheme of DMPT-1 and DMPT-2 ligands [181].

Both compounds do not exhibit high thermal stability, they decompose exothermically at 191 and 206 °C, respectively. This is attributed to the presence of a C-NO_2 bond in the molecule, which can weaken the structure of the molecule, causing it to decompose at lower temperatures [182]. DMPT-1 and DMPT-2 can be considered as compounds that are not very sensitive to impact and friction - in the case of impact sensitivity, for both compounds, the value is 30 J, while in the case of friction sensitivity, 108 and 192 N, respectively. The authors of the paper [181] also calculated the detonation parameters, which show that the compound DMPT-1 at a density of 1.806 g/cm^3, reaches a detonation pressure of 30.2 GPa and a detonation velocity of 8610 m/s, while DMPT-2 at a density of 1.77 g/cm^3, reaches a detonation pressure of 28.06 GPa and a detonation velocity of 8450 m/s. Despite the fact that these are calculated values, the use of methylene bridge in the design of new energetic materials, is promising. However, to date, energetic coordination compounds containing DMPT-1 and DMPT-2 as potential ligands have not been synthesised.

3.5. Energetic coordination compounds containing oxadiazoles

Another group of compounds that can be employed as ligands in energetic coordination compounds are oxadiazoles, which belong to the group of heterocyclic compounds containing two nitrogen atoms and one oxygen atom in the ring. The compound has four isomers in the form: 1,2,3-, 1,2,4-, 1,2,5- and 1,3,4-oxadiazoles (Fig. 34) [183]. The most commonly described isomers in the literature are 1,2,4- and 1,3,5-oxadiazoles, in turn, the least stable are the 1,2,3-oxadiazole compounds, which are usually found in the diazoketone tautomeric form [184]. Compounds based on 1,2,5-oxadiazoles are considered to be the most stable isomers of the oxadiazoles,

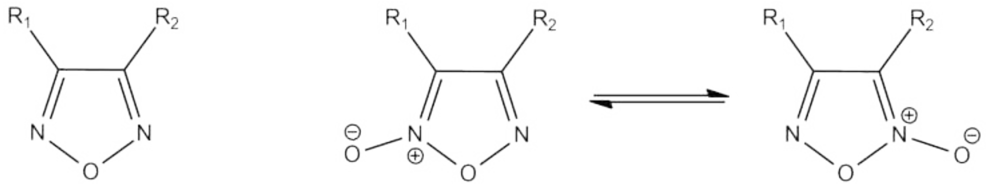
189 **190** **191** **192**

Figure 34: Structure of oxadiazole isomers.

Oxadiazole-based molecules, apart from their energetic properties, exhibit a wide spectrum of biological properties, e.g. antimicrobial activity and and have been used in the fight against cancer, inflammation or diabetes (such as ataluren and zibotentan) [183]. These compounds may also be components of herbicides, pesticides or components of dyes and liquid crystals [185].

Oxadiazoles, like triazoles or tetrazoles, are capable of attaching various functional groups such as amino, nitro, which increases the amount of nitrogen in the molecule, infuencing on detonation performance. For example, these may include compounds containing nitro- and nitramine monofurazans, chain furazans, macrocyclic furazans and furazans with rings connected by bridges of azo groups.

Furazane as well as furoxane (N-oxide derivative) (Figure 35) are a widely investigated group of compounds. These compounds, in themselves, exhibit explosive properties. They posses high nitrogen and oxygen contents which are 62.8 wt. % and 69.7 wt. % , respectively [186]. These compounds have a high electron density due to the distribution of six electrons on five atoms [187]. Given the presence of two tautomers, 2-oxy and 5-oxy, furoxane is a less stable compound.



furazan **furoxan**

Figure 35: Structures of furazan and furoxan [186].

The poly structures of furazane and furoxane can be linked by carbon-carbon bonds, oxygen atoms, nitrogen atoms, azo and azoxy bridging, or a combination of these (e.g., azo/azoxy and heteroatoms linkers, azo/azoxy and carbon-carbon bonds) [186]. The use of the aforementioned bridging links results in the formation of larger molecules, conjugated systems that increase the rigidity of the molecule and, therefore, influence the assurance of greater stability of the system leading, for example, to greater thermal stability. The figure below shows examples of compounds linked by a carbon-carbon bond (Fig. 36), for which 3,3'-Diamino-4,4'-bifurazane (DAAF) and 3,3'-diamino-4,4'-bisfuroxane are treated as precursors.

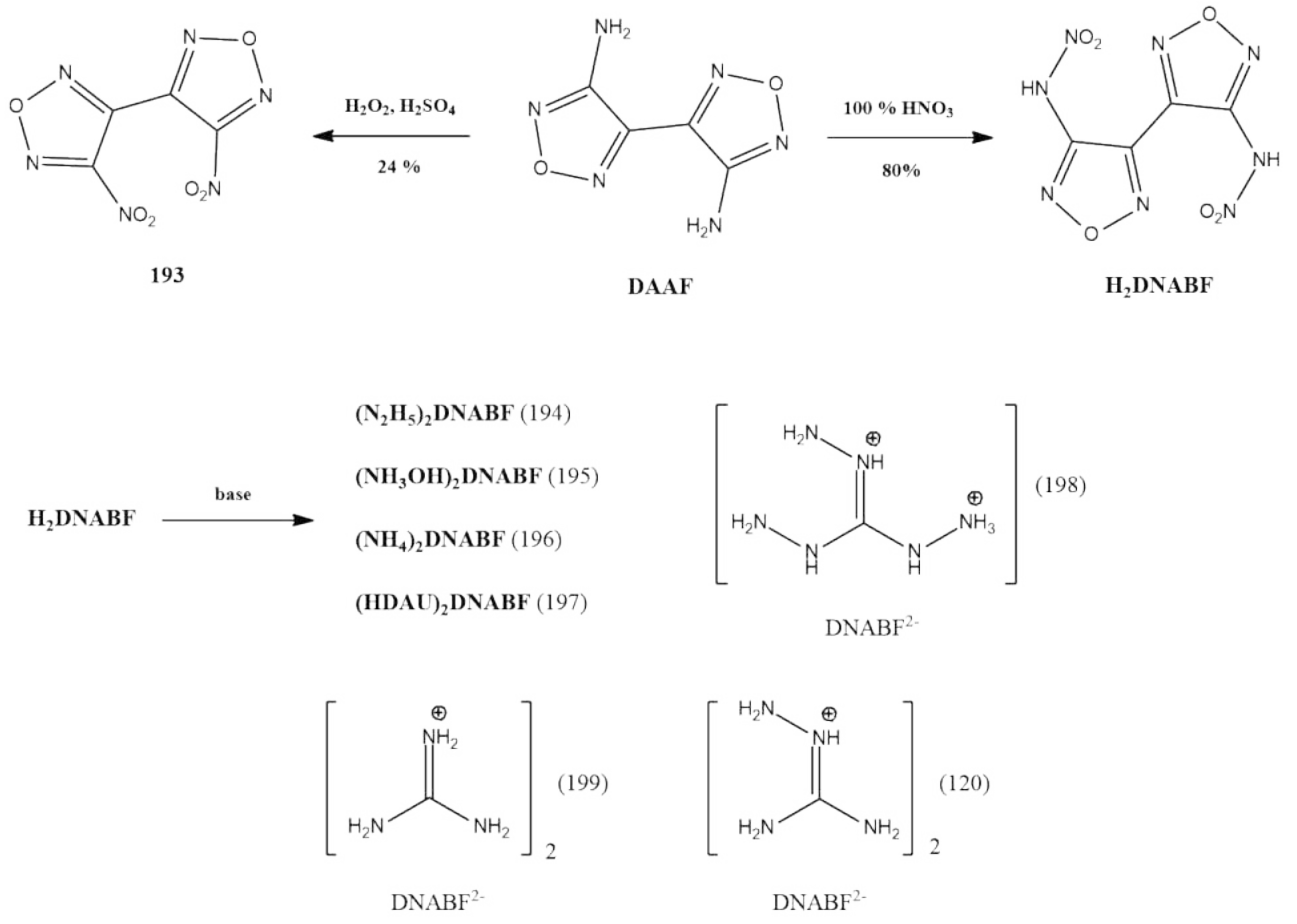


Figure 36: Synthesis scheme of carbon-carbon linked oxadiazoles [186].

DAAF can be obtained in two ways. The first way is a cyclization reaction using dichloroglyoxime, dicyanoglyoxime and tetraoxymodiaminobutane. Another way is a one-step reaction using isocyanilic acid [188]. Oxidation of DAAF using H_2O_2/H_2SO_4 leads to the formation of 3,3'-dinitro-4,4'-bifurazane. The following table shows the physicochemical and detonation parameters of the compounds obtained by the authors of the paper.

Table 21: Sensitivity and detonation parameters for CC bridge oxadiazoles [186].

Compound	ρ **[g/cm^3]**	**T$_{dec.}$ [°C]**	**IS [J]**	**FS [N]**	**P [GPa]**	**D [m/s]**
H$_2$DNABF	1.94	80	1.5	48	40.3	9086
194	1.78	230	6	120	35.4	9058
195	1.93	141	11	288	42.5	9363
196	1.80	230	10	324	33.4	8748
197	1.78	192	40	360	33.3	8848
198	1.81	203	3	360	33.5	8836
199	1.72	280	40	360	27.1	8225
200	1.65	215	10	360	26.5	8228

Most compounds have high thermal stability, with an exothermic decomposition temperature of more than 200 °C with the exception of H$_2$DNABF (80 °C), compound **(195)** (141 °C) and compound **(197)** (192 °C). Among the mentioned compounds, H$_2$DNABF is the most sensitive compound to impact and friction, reaching values of 1.5 J and 48 N. It also achieves the highest pressure and detonation velocity. The least sensitive to impact and friction are compounds 11 and 13.

It is also possible to form poly-furoxane structures such as DNTF, which contains in the structure three rings of 1,2,5-oxadiazole, and its derivatives [189,190]. The heat of formation of DNTF is 657 kJ/mol, making it a more energetic compound than 2,4,6-trinitrotoluene (TNT). In the synthesis of new energetic materials, or in the design of new materials, the literature reports the possibility of modifying compounds by combining the nitro group with azo groups, thereby improving the energy parameters of the compounds [191]. In addition to the nitro group, which is an explosophoric group, an example of such a combination can be the insertion of, for instance, a poly-azotroalkyl-ONN group. It is also possible to replace the nitro groups with trinitromethyl-ONN-azoxy and fluoronitromethyl-ONN-azoxy groups, thereby improving the detonation properties.

It is also possible to obtain more compounded energetic compounds containing both 1,2,4-oxadiazole and 1,2,5-oxadiazole isomers in the backbone, along with -ONO$_2$ and -NHNO$_2$ groups [192]. The authors of this paper obtained a number of compounds of this type: 3-nitramino-4-(5-hydroxymethyl-1,2,4-oxadiazol-3-yl)-furazane **(201)**, 3,3'-bis[5-nitroxymethyl-1,2,4-oxadiazol-3-yl]-4,4'-azofuroxane **(202)**, [3-(4-nitroamino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-yl]-methylene nitrate **(203)** as well as energetic ionic salts **(204-206)**. The introduction of the -ONO$_2$ group improves the detonation parameters of the target compounds, increasing their density. On the other hand, the O−N bond present in this group is a weak bond due to having an unbalanced electrostatic potential surface, consequently providing low thermal stability of aliphatic nitrate esters [193]. The structures of abovementioned compounds is shown in figure below (Fig. 37).

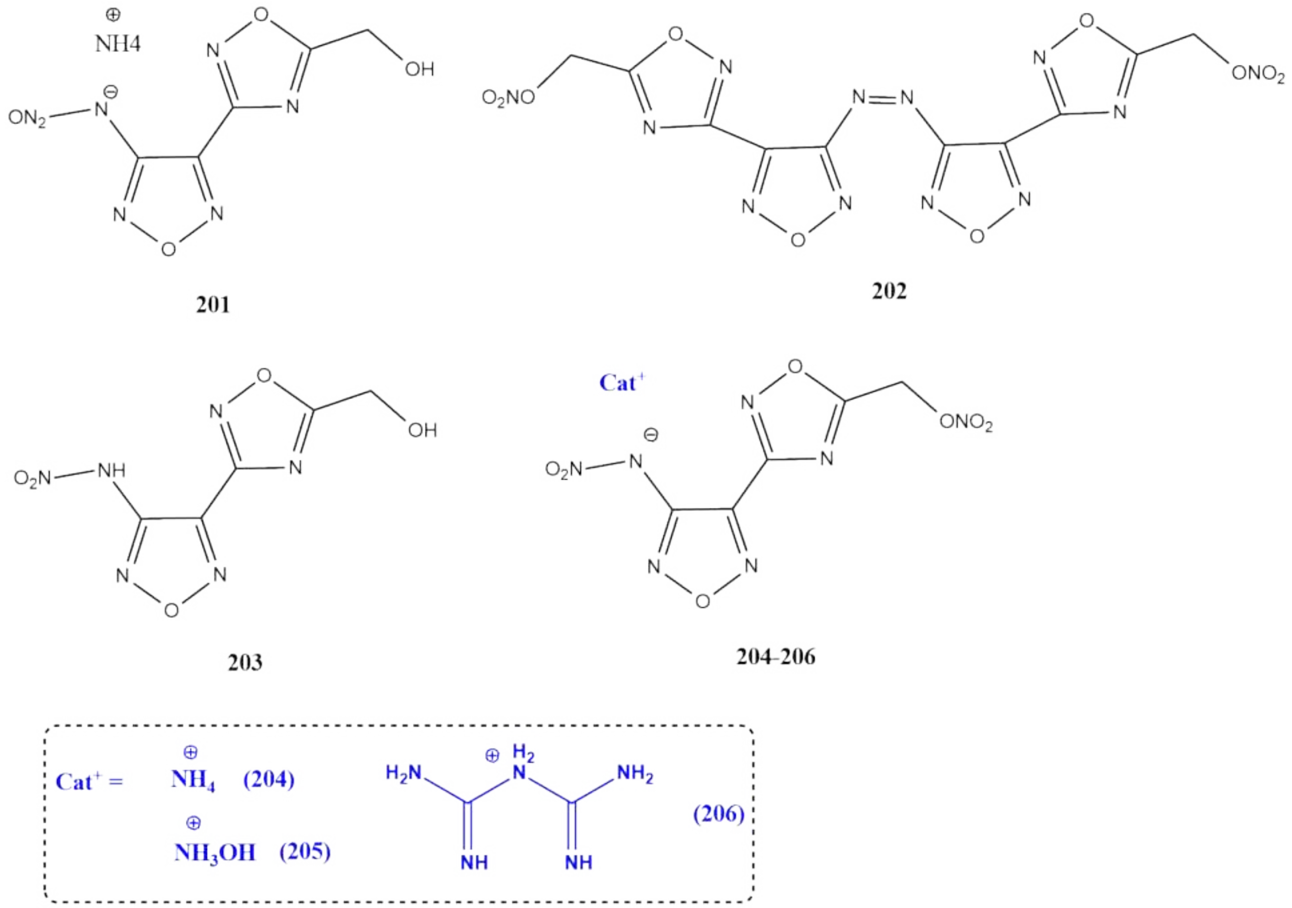


Figure 37: Examples energetic compounds containing both 1,2,4-oxadiazole and 1,2,5-oxadiazole isomers.

The authors of the work determined the thermal stability and also the sensitivity parameters of the obtained compounds, which were shown in Table below (Tab. 22).

Table 22: Physiochemical and energetic properties of compounds containing 1,2,4-oxadiazole and 1,2,5-oxadiazole isomers.

Compound	ρ **[g/cm^3]**	**T $_{\text{dec.}}$ [°C]**	**IS [J]**	**FS [N]**	**P [GPa]**	**D [m/s]**
202	1.78	200	35	> 360	27.4	8081
203	1.83	60	10	-	31.1	8451
204	1.79	135	35	> 360	32	8428
205	1.82	148	40	> 360	35.2	8822
206	1.75	135	> 40	> 360	27.2	7809

All compounds have low thermal stability and decompose exothermically at temperatures below 150 °C except compound **(203)**, which decomposes at 200 °C. In addition, the compounds exhibit no friction sensitivity (> 360 N) and friction and low impact sensitivity (35 to > 40 J) apart from compound **(203)** (10 J). The calculated detonation parameters are in the range, with pressures of 27.2 and 35.2 GPa and detonation velocities in the range of 7809 and 8822 m/s. Of these compounds, the optimal parameters were achieved by compound **(205)**, comparably for RDX parameters.

There are also oxadiazole-based compounds, which are azo linked (Fig. 38). As well as introducing an amino group into the furazane molecule, it is possible to obtain a molecule containing a nitrofurazane linked by an azo bridge and also obtain molecule with trifurazane structure [185]. The precursor of these compounds is 3,3'-diamino-4,4'-azofurazane (DAAzF), which is determined as a non-sensitive explosive.

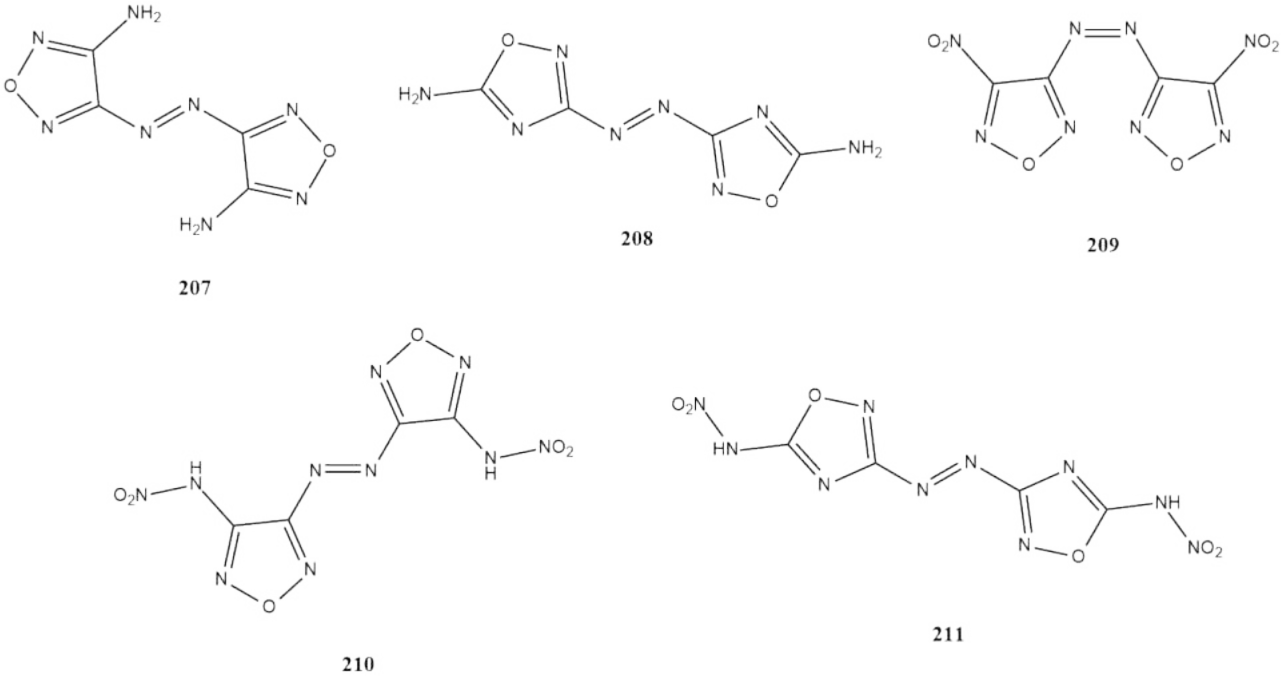


Figure 38: Examples of azo bridge oxadiazole compounds.

The isomer of DAAzF is compound **(208)**, which has 1,2,4-oxadiazole in its structure instead of 1,2,5-oxadiazole. The location of the substituents in a different position of the ring, affects the properties of this compound. One of the parameters distinguishing the two isomers is thermal stabilities. DAAzF decomposes exothermically at temperature 320 °C, in turn **(208)** decomposes at temperature 355 °C. Nitration of DAAzF with 100 % nitric acid yields a molecule enriched in a nitro group **(209)**, while nitration of compound **(208)** yields compound **(211)** (Fig. 38).

Because compounds containing oxadiazoles are themselves energetic molecules, the literature does not indicate the occurrence of a large number of energetic transition metal coordination compounds.

The authors of the paper [194] indicate the presence of coordination compounds containing derivatives of 2,5-disubstituted-1,3,4-oxadiazoles - ligands in the form of 2-(furan-2-yl)-5-(pyridin-2-yl)-1, 3,4-oxadiazoles (fpo) and 2-(pyridin-2-yl)-5-(thiophen-2-yl)-1,3,4-oxadiazoles (pto) with Fe(II) and Co(II) metals. This compounds can exist in *cis-* and *trans-* configurations. The coordination compounds can be assigned to the general formula $[M(L)_2(NCS)_2]$ (where **(212)** - M = Co, L = fpo; **(213)** - M = Co, L = tpo; **(214)** - M = Fe, L=fpo; **(215)** - M=Fe, L=tpo). Structural studies showed that compounds **(212)** and **(214)** exhibit a monoclinic crystal system and also preferentially occur in the cis configuration, while compound **(213)** exhibits a triclinic crystal system with a trans configuration. However, the focus of this paper is on determining the magnetic properties, not considering the detonation parameters.

On the other hand, the authors of the paper [195] obtained coordination compounds containing 2-amino-5-substituted aryl-1,3,4-oxadiazole with Cu(II). The synthesis involved mixing an ethanolic solution of the ligand with hydrated copper(II) sulfate and then refluxing the resulting mixture. In order to purify the obtained compound and separate the unreacted ligand, or salt, the solution was filtered and then washed with water and ethanol. Thermal analysis of the obtained compound was carried out, which showed that after the loss of water at about 100 °C (endothermic decomposition), the molecule loses coordinated water in the temperature range of 250 – 280 °C and the complete exothermic decomposition of the compound occurs in the temperature range of 420 – 470 °C, indicating high thermal stability. However, the authors of the paper did not characterise the compound for use in high-energy coordination compounds, but only determined the magnetic properties and antimicrobial use.

Another example is the transition metal coordination compounds obtained by the authors of the paper [196] containing 5-(2-phenyl-4-pyridyl)-1,3,4-oxadiazole-2-thione (ppot) with the general formula $[M(ppot)_2Cl_2(H_2O)_2]$ (where M = Cu(II), Co(II), Ni(II) and Zn(II)). The synthesis of the compounds involved preparing a solution of the corresponding metal chloride containing ethanol and water at 60 °C and adding it with a solution of carbodithioate also containing ethanol and water at the same temperature. The reaction was carried out under a reflux and after its completion the precipitate was filtered off and washed with a solution of ethanol and water in a molar ratio of 1:1. Thermal analysis was carried out for the obtained compounds, which indicated a two-stage decomposition - the first - endothermic, associated with the loss of water, the next - exothermic associated with the decomposition of the whole molecule (decomposition in the temperature range 360 - 520 °C). As in previously described cases, the authors of the paper also characterised the compounds by their antibacterial properties.

4. THEORETICAL FOUNDATIONS OF UTILISED INSTRUMENTAL METHODS

4.1. INFRARED SPECTROSCOPY

Infrared spectroscopy provides information about the structure of molecules being investigated and their interactions with their environment. The interaction of an electromagnetic wave with matter causes a change in internal energy (conservation of energy principle), which is expressed by the formula:

$$\Delta E = h \cdot \nu = h \cdot \frac{c}{\lambda} \tag{1}$$

Where:

h - Planck's constant ($6.63 \cdot 10^{-34}$ [J·s])

ν - frequency

c - spped of light (in a vacuum $3 \cdot 10^{8}$ m/s)

λ - radiation wavelength

This formula defines the relationship between the absorbed energy and the frequency or wavelength of the induced transition. The relationship between the energy of the radiation transmitted, absorbed or emitted and the wavelength, electromagnetic wavelength or frequency is expressed in transmission, absorption or emission, respectively. The measure of radiation absorption is expressed in transmittance (T) or absorbance (A) [197]. Δ E is the difference in energy absorbed during the transition in a molecule from a lower energy state, the ground state, to a higher energy state, the excited state. The absorbed energy depends in turn on the energy difference between the ground and excited states - the smaller the energy difference, the longer the wavelength. The formula (1) also shows that Δ E is directly proportional to frequency and wave number and inversely proportional to wavelength, which is why in spectroscopy energy is expressed in cm^{-1} (unit of frequency). In the case of IR spectra, it is possible to observe only those oscillations which are accompanied by a change in the dipole moment of the molecule [198].

During the measurement, the electromagnetic radiation (in the IR range) that passes through the sample has a frequency similar to that of the vibrations of the particles. As a result of selective absorption of the radiation, the amplitude of vibration in the molecules increases; in turn, absorption of the radiation is accompanied by changes in the rotational and oscillatory energy of the molecules. Because this energy is quantised, only radiation with energies, which are characteristic for the functional groups performing the vibrations, is absorbed.

In this way, the technique makes it possible to determine the characteristic functional groups involved in a molecule. Oscillatory levels are associated with the oscillatory motion of nuclei in molecules around equilibrium positions (the energies of these oscillations are 0.02 - 0.05 eV), while rotational levels of molecules are associated with the rotational motion of molecules (the energy changes are of the order of fractions of an eV, i.e. within the range of about 100 - 0.1 cm^{-1}).

The spectrum obtained shows the dependence of the absorption on the radiation energy. The resulting spectrum shows the dependence of the absorption on the radiation energy. The radiation intensity (I), transmittance and absorbance are related by the following dependence:

$$T(\nu) = \frac{I}{I_0} \tag{2}$$

$$A(\nu) = log\frac{I_0}{I} = -logT \tag{3}$$

The formula indicates that the absorbance within the linearity range of Lambert-Beer's law is directly proportional to the concentration of the absorbing molecules.

One of IR techniques is the attenuated total reflection (ATR) method [199], which was used within the work. In this technique, a beam of infrared radiation is introduced into an infrared transparent material with a high refractive index and falls on its inner surface, for example diamond. Long crystals (e.g. of zinc selenide or germanium) are used to increase the intensity of the signal. The tested sample at the point of reflection adheres to the outer side of this surface. During the measurement, the beam undergoes multiple internal reflections at a certain angle and then comes out on the other side. For the radiation to be completely internally reflected, the angle of incidence must be greater than the critical angle. The intensity of a beam is measured as a function of its wave number after it has been withdrawn from a medium in which total internal reflection has occurred.

4.2. RAMAN SPECTROSCOPY

Raman spectroscopy is an instrumental analysis method for obtaining information about the vibrational properties of molecules, by measuring Raman scattering radiation, i.e. inelastic scattering of photons [200]. A characteristic feature of Raman spectra is the change in the frequency of the scattered radiation (ν_{r}) relative to the frequency of the incident radiation (ν_{p}), which is represented by the following formula:

$$\nu_{\mathrm{r}} = \nu_{\mathrm{p}} + \nu \tag{4}$$

Where:

ν - transition frequency for the scattering system

When photons are incident on a given system with an energy significantly higher than the energy corresponding to the difference between the oscillatory levels, and simultaneously lower than the energy corresponding to the difference between the fundamental electron level and the first excited electron level of the molecule, it undergoes scattering.

In Raman spectroscopy, three selection rules must be maintained. Firstly, the ΔE difference for the incident and scattered photon must be consistent with the oscillation level difference $\Delta E = h\nu_0 - h\nu_r$. Secondly, for a harmonic oscillator, there is a quantum change in the oscillation with $\Delta\ \nu = \pm\ 1$ during the transition. For anharmonic oscillator $\Delta\ \nu = \pm\ 1, \pm\ 2, \pm\ 3$. Finally, it is assumed that during the oscillation there is a change in the polarisability of the particle [201], derived from transitions between quantum states (changing the dipole moment).

The measurement is based on directing a beam of monochromatic radiation at the test sample at an angle of 90°, preventing reflection. Since the range of radiation does not correspond to the difference in the energy of transitions between the energy levels of the molecule, there is a scattering of the beam, which is caused by the induction of the dipole moment of the molecule that becomes a source of radiation, emitted in all directions. In the spectra, we record scattered radiation and the observed frequency shift provides information about the distances of the energy levels

4.3. Scanning Electron Microscopy

Scanning electron microscopy is a method that employs an electron beam to observe and analyze the surface of samples. The resulting image is the result of the detector's registration of secondary and backscattered electrons formed by the incident electron beam on the sample. Secondary electrons are produced by inelastic interactions.

In order for an electron beam to form, an electron source is required, as well as an electrostatic field in which electrons are accelerated due to the potential difference between the cathode and anode. The electron source is the cathode, while the particles are accelerated by their attracting to the anode [202]. In order for ensure stability of the beam, it is necessary to provide a vacuum, because in the absence of vacuum, electrons lose kinetic energy through collisions with gas particles. Electrons are particle-wave in nature and the wavelength depends on the momentum achieved in the electrostatic field, according to the following equation:

$$\lambda = \frac{h}{p} \tag{5}$$

Where:

λ - wavelength

h - Planck's constant ($6.63 \cdot 10^{-34}$ [J·s]) p = m · v - momentum of the electron

The kinetic energy, meanwhile, depends on the potential difference between the cathode and anode and is called the accelerating voltage. Taking this factor into account in the equation (5), the relationship is obtained:

$$\lambda = \frac{h}{\sqrt{2m \cdot e \cdot U}} \tag{6}$$

Where:

h - electron charge

m - mass of the electron

U - accelerating voltage

By introducing a relativistic correction to equation (6), the following equation is obtained:

$$\lambda = \frac{h}{\sqrt{2m_0 \cdot e \cdot U(1 + \frac{e \cdot U}{2m_0 c^2})}} \tag{7}$$

Where:

m_0 - rest mass of the electron

c - spped of light

An important phenomenon that occurs is inelastic scattering, associated with the loss of kinetic energy of the beam electrons. In this case, the intensity of the radiation beam is calculated according to the formula:

$$I = I_0 \cdot exp(-c \cdot \rho \cdot d) \tag{8}$$

Where:

I - incident beam intensity

c - constant proportional to the ratio Z/A (Z - atomic number, A - mass number) dependent on the accelerating voltage

ρ - material density

d - the thickness of the product

The principle of the scanning electron microscope is to form a beam of electrons that falls on the sample and produces various effects. As a result of the collision of electrons with atoms, electrons lose their kinetic energy, resulting in emission of radiation or undergo elastic "reflection", as well as pass through the sample. The result of the interaction of incident electrons with the electrons of the sample's atoms is the emission of secondary electrons, backscattered electrons, Auger electrons, or X-rays, fluorescence radiation [202]. Each type of radiation is emitted from a different depth and volume of the material under investigated, which increases as the accelerating voltage increases.

4.4. X-RAY DIFFRACTOMETRY

A diffraction method such as XRD is used to investigate the structure of solids by determining the crystalline phases [203]. In X-ray diffraction, Bragg's law is applied, which can be described according to the formula below:

$$n \cdot \lambda = 2d \cdot sin\theta \tag{9}$$

Where:

n - deflection row

λ - wavelength

d - interplanar distance

θ - beam deflection angle

The method is based on the phenomenon of diffraction of an electromagnetic radiation beam whose length is similar to the interplanar distance in the crystal lattice. In the case of X-rays, these are generated by a cathode ray tube and are then filtered to obtain monochromatic radiation. Such radiation is then collimated and directed towards the material under investigation. After contact with the material, the beam of radiation incident on the material meets an ordered network of atoms/particles, behaving as a diffraction grating. Depending on the absorption coefficient of the material under test and also the wavelength of the incident beam, a partial energy loss of the radiation beam is possible, resulting from the absorption of energy by the electrons of the atoms of the material under test. The beam can also scatter to form multiple beams. As a result, the radiation beam may scatter with a change in wavelength - incoherent scattering, or without a change in wavelength - coherent scattering, which is more common. In turn, the occurrence of different phases is related to the plane of reflection, on which the path travelled by the radiation beam depends [204].

4.5. ELECTROCHEMICAL ANALYSIS - CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) is a techniqe that measures the current flowing through a working electrode as a function of the potential applied to it. A cyclically varying potential difference is forced between the working electrode (WE) and the reference electrode (RE). The working electrode is the electrode at which the redox reaction takes place, determining the potential at which the electrode reaction takes place and whether the process is classified as reversible or irreversible. This electrode can be made of metals such as Au, Pt, Ag or glassy carbon

[205]. There are also working liquid electrodes with a surface that renews itself continuously or periodically, such as a dropping mercury electrode. Reference electrode (RE) is an electrode against which the potential of the working electrode is measured. A characteristic of the reference electrode is its non-polarity, resulting in no change in potential as a result of flowing current. A component of the three-electrode system is also the counter-electrode (CE), which ensures that the potential of the reference electrode remains constant.

During the measurement, current flows between the working electrode and the reference electrode, in turn the potential of the working electrode is measured by means of a potentiostat relative to the reference electrode. The potentiostat provides the EC polarisation and the measurement of the current flowing between it and the CE [206].

Considering the simplest electrode processes, they are likely to be divided into three stages. In the first stage, an electroactive substance is brought to the electrode surface. In the next stage, an electrode reaction takes place over time involving the transfer of electrons from the electroactive substance to the electrode, where the oxidation process takes place, or from the electrode to the electroactive substance, where the reduction process takes place [207]. In the third stage, as a result of diffusion, the product of the electrode reaction moves into solution or is deposited on the surface of the working electrode and the measured current is the diffusion current.

By knowing the oxidation and reduction peak potentials, it allows the formal potential (E_0) to be determined according to the following equation:

$$E_0 = \frac{E_{ox} + E_{red}}{2} [V] \tag{10}$$

Where:

E_0 - redox couple potential Fc/Fc^+,

E_{ox} - oxidation potential of ferrocene relative to the reference electrode

E_{red} - reduction potential of the ferrocene cation relative to the reference electrode

Reversible processes (at 298 K) are related by the relationship:

$$E_{1/2} - E^0 = (\frac{2.20RT}{nF}) = \frac{0.0565}{n} [V] \tag{11}$$

In turn, the peak current value of an electrode reaction taking place under diffusion conditions for a reversible reaction is described by the Randles-Sevčik equation [208]:

$$I_{\mathrm{p}} = 0.446nFAc\sqrt{\frac{nF\nu D}{RT}} [A] \tag{12}$$

Where:

I_p - peak current [A]

n - number of electrons exchanged in the electrode process

F - Faraday's constant, F = 9.6485 [c/mol]

A - working electrode surface [cm^3]

c - concentration of depolariser in the depth of the solution [mol/cm^3]

ν - speed of potential change [V/s]

D - depolariser diffusion coefficient [cm^2/s]

R - gas constant, R = 8.314 [J/(mol·K]

T - temperature [K]

The use of cyclic voltammetry provides information on the reversibility of the process (process kinetics), the adsorption process on the electrode and the identification of the reaction mechanism.

4.6. SENSITIVITY TO MECHANICAL STIMULI

Sensitivity to friction

Testing the friction sensitivity of energetic materials can be carried out by several methods, the examples which are the ABL friction test and the BAM friction test, which is most commonly performed in Europe [209]. Another method is to determine the value of the load causing 50 % of the reaction of the material under test (h_{50}). The result obtained is considered the average value of friction sensitivity. This method is mainly employed in the United States and Asia [210].

Within the work, the friction test is carried out using a friction apparatus (Peters apparatus) in accordance to the international standard EN 13631-3:2005 [211]. The measurement method involves placing the tested material on a porcelain plate and a porcelain peg is pressed onto the sample under a specified load. The cylindrical peg is fixed in the holder of the loading device, in turn, the load amount is adjusted by suspending weights of different weights in different notches of the loading arm by a ring and hook. When the switch is turned on, the plate is moved in two directions in an electromechanical manner relative to the stationary punch, which causes friction between the porcelain plate and peg. The test is carried out from the highest load (360 N), in the direction of the smaller ones, until no reaction is observed. The occurrence of a reaction indicates the appearance of a bang, crackle, sparks or flame.

This method allows determining the load on the test specimen in the range from 360 to 5 N. It is possible to test substances in the form of solids and powders, plastic-bonded substances and also substances in the form of paste and gel-like type.

Friction sensitivity is defined as the smallest load at which a reaction occurs in at least one of the six trials. Based on the abovementioned standard, it is possible to determine the upper limit of insensitivity, which determines the maximum load that does not cause a reaction in the tested material, and the lower limit of sensitivity, which determines the minimum load that causes a reaction in the tested material. Real friction sensitivity values are between these two values.

Sensitivity to impact

The impact sensitivity test is carried out using an impact apparatus/fall hammer, usually according to BAM. In Europe, such testing is most commonly performed in accordance with the international standard EN 13631-4:2004 [212]. The determination of impact sensitivity is related to the determination of the lowest impact energy at which one response is obtained in at least six tests. Similar to friction sensitivity testing, an upper limit of insensitivity and a lower limit of sensitivity are determined. The impact sensitivity test is based on the fall of a weight of a given mass on the material sample being tested, which is closed in such a way as not to cause friction of the material during the impact of the weight. The occurrence of a reaction is considered to be the appearance of a flame or a sound effect, and the result of the reaction is marked as "+" or "-". To calculate the energy of the impact, the value of the standard gravity is rounded up to 10 m/s. It is also possible to determine the value of the fall that causes a 50 % firing rate of the tested compound. The value obtained is considered the average value of impact sensitivity. As with the determination of friction sensitivity, this method is mainly used in the United States and Asia [210].

4.7. THERMOCHEMICAL STUDIES

Determination of ignition/explosion temperature

Determining the sensitivity of explosives to thermal stimuli allows to characterise them in terms of safety of production, transportation, storage and, especially, application. As a result of the supply of energy in the form of heat and the associated increase in the temperature of the material under test, ignition or auto-ignition occurs. The ignition temperature determines the lowest temperature to which a liquid must be heated, at which the amount of vapor released reaches such a concentration above the surface of the material at which a flammable mixture with air is formed. The auto-ignition temperature, meanwhile, determines the lowest temperature to which a substance must be heated in order for it to be capable of spontaneous ignition in the presence of oxygen.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a technique that allows the measurement of the difference in the amount of heat required to achieve a linear increase or decrease in the temperature of a test sample as a function of temperature. This technique indicates that physical transformations (e.g. phase transitions) take place during the gradual heating of the sample - exothermic processes such as crystallisation or endothermic processes such as melting take place in the sample.

4.8. Determination of detonation parameters

There are classical methods of determining relative work capacity such as detonation in a lead block (Trauzl block) or the use of a ballistic pendulum. However, these methods require the use of a larger amount of explosives between 10 to 20 g. It is also possible to use the method of testing the detonation capability of an underwater explosion test to determine the detonation pressure and velocity. The classical method involves testing in large tanks, pools with dimensions of at least: 24 × 24 × 13.5 m and load immersion depth of at least 2.7 m [210]. To carry out the tests, it is necessary to use piezoelectric sensors that allow recording with an oscilloscope the shock wave propagating in the water and the time of collapse of the gas bubble of the explosion products. It is also possible to perform tests in tanks of smaller volume (1 m^3), according to EN 13763-15 [213], using a smaller amount of materials and similarly piezoelectric sensor. The oscillogram obtained as a result of the measurements in the form of the function $E = f(t)$ allows to determine the shock wave pressure by calculating it based on characteristics of the sensor and the equivalent energy of the shock wave and the equivalent energy of the gas bubble.

In an underwater explosion, the explosive releases its energy into shock wave energy, bubble energy and thermal energy loss as a result of detonation underwater due to the compression of the water medium. The shock wave in water is generated by the crossing of the detonation wave from the charge into the surrounding medium, where it is further propagated. The secondary pressure wave is associated with first collapse of gas bubble. Important parameters affecting the effectiveness of the materials are the peak shock wave pressure obtained, the bubble period, the damping time constant, the shock wave pulse, as well as the energy and energy flux density [214]. The shock wave in water is generated by the crossing of the detonation wave from the charge into the surrounding medium, where it is further propagated. The secondary pressure wave is associated with first collapse of gas bubble.

According to the standard [213], the test assumes the determination of two coefficients (also reffered as equivalents) - the shock wave energy equivalent (E_{SW}) and also bubble gas energy equivalent (E_{BW}), according to the formulas below (Equation 13 and 17).

Based on output voltage from the pressure sensor, the intergral under the squared pressure/time curve may ba calculated:

$$E_{\mathrm{SW}} = \frac{4\pi * R_2}{\rho_{\mathrm{water}} * C_{\mathrm{water}}} \int_{t_0}^{\theta} p^2 \, dt \tag{13}$$

Where:

E_{SW} - shock wave energy equivalence [J];

ρ_{water} - water density g/cm^3;

C_{water} - sound velocity in water;

R_2 - distance between detonator and pressure sensor;

θ - (p_{max}/e);

p - pressure [Pa]

Bubble pulse energy equivalence is related with pulse time by equation:

$$t_{\mathrm{B}} = \frac{1.135 \cdot \sqrt{\rho_{\mathrm{water}}} \cdot \sqrt[3]{E_{\mathrm{BW}}}}{\sqrt[6]{p_{\mathrm{h}}{}^5}} = \frac{1.135 \cdot \sqrt{\rho_{\mathrm{water}}} \cdot \sqrt[3]{E_{\mathrm{BW}}}}{\sqrt[6]{(g \cdot h \cdot \rho_{\mathrm{water}} + 101325)^5}} \tag{14}$$

Where:

t_B - time between pressure peak and first bubble collapse [ms];

E_{BW} - bubble pulse energy equivalence [J];

p_h - hydrostatic pressure [Pa];

g - free fall acceleration = 9.81[m/s^2];

h - depth of detonator immersion [m].

The equation (14), for constant conditions may be simplify to:

$$\frac{t_{\mathrm{B}}}{K_1} = \sqrt[3]{E_{\mathrm{BW}}} \tag{15}$$

$$\frac{t_{\mathrm{b}}}{K1} = \sqrt[3]{E_{\mathrm{BW}}} \tag{16}$$

The bubble energy may be calculated based od the time interval between the shock-wave pressure peak and the first collapse of the gas bubble created from the detonation gasses. After transforming the equation 16, the bubble gas energy equivalent is defined as:

$$E_{\mathrm{BW}} = (\frac{t_{\mathrm{b}}}{K1})^3 \tag{17}$$

Where:

K_1 - equal for our system to 23.14·10^{-4}, is described with equation:

$$K_1 = \frac{1.135 \cdot \sqrt{\rho_{\mathrm{water}}}}{\sqrt[6]{(g \cdot h \cdot \rho_{\mathrm{water}} + 101325)^5}} \tag{18}$$

The total energy of the explosion is the sum of shock wave energy equivalent and bubble gas energy equivalent:

$$E = E_{\mathrm{SW}} + E_{\mathrm{BW}} \tag{19}$$

5. EXPERIMENTAL SECTION

5.1. SYNTHESIS

Chemicals

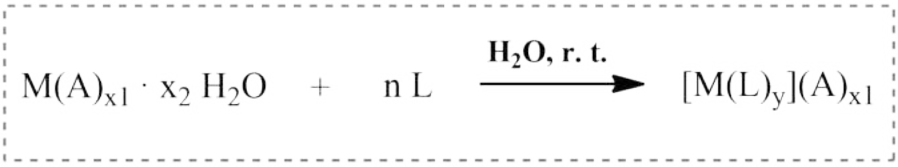
The reagents used in this work (Tab. 23) have been used as received from the indicated suppliers without further purification.

Table 23: Chemicals used in the syntheses.

Chemical	**Purity [%]**	**Source**
Iron(III) nitrate nonahydrate	≥ 98	Sigma-Aldrich
Nickel(II) nitrate hexahydrate	≥ 98.5	Sigma-Aldrich
Copper(II) nitrate hemi(pentahydrate)	> 98	Sigma-Aldrich
Zinc nitrate hexahydrate	> 98	Sigma-Aldrich
Iron(II) perchlorate hydrate	> 98	Sigma-Aldrich
Nickel(II) perchlorate hexahydrate	> 98	Sigma-Aldrich
Copper(II) perchlorate hexahydrate	> 98	Sigma-Aldrich
Zinc perchlorate hexahydrate	> 98	Sigma-Aldrich
1,2-ethylenediamine	> 99	Chemsolve
1,3-diaminopropane	> 98	TCI
Tris(2-aminoethyl)amine	> 98	TCI
Tris(3-aminopropyl)amine	> 97	TCI
Acetone	≥ 99.5	Sigma-Aldrich
Ethanol 96 %	cz.d.a.	Stanlab
N,N-dimethylformamide	≥ 99.8	Eurochem
Ferrocene	98	Acros Organics
Tetrabutylammonium tetrafluoroborate	98	TCI

Synthesis procedure

Into a 150 cm^3 round-bottom flask placed in a water bath equipped with a mechanical stirrer with a glass stirring rod, the corresponding metal salt and water were introduced. The salt solution was stirred for 10 minutes until the salt was completely dissolved. Then, at room temperature, the addition of the selected ligand was started in small portions for 45 minutes at 15-minute intervals (during the addition of successive portions of the ligand, the color change of the solution can be observed). After adding the entire portion of the ligand, the reaction mixture was stirred for 30 minutes. The resulting solution was transferred to a rotary evaporator and evaporated to dryness under reduced pressure. The obtained product was washed with ethanol. After evaporation of the solvent, the resulting product was dried at 60 °C for 4 h. In order to purify unreacted reagents, the compounds obtained were washed three times with acetone (1.5 ml of acetone each) and then left at room temperature until the solvent evaporated completely. The following figure (Fig. 39) shows the general synthesis scheme.



Where:

M - Fe, Ni, Cu, Zn
L - EDA, DP, TAEA, TAPA
A - NO_3^-, ClO_4^-
x_1 - metal value
x_2 - number of molecules
n - number of moles

Figure 39: Synthesis scheme for obtaining the energetic coordination compounds.

For the synthesis of ECCs, as a ligand 1,2-ethylenediamine; 1,3-diaminopropane; tris(2-aminoethyl)amine and tris(3-aminopropyl)amine were used, as well as nitrates of transition metal salts containing Fe, Ni, Cu, Zn and their perchlorate analogues. Due to the non-toxic nature and good solubility of metal salts and ligands in water, water was chosen as the reaction medium.

The following tables show the amounts of reactants used for synthesis, calculated per 1 g of product and yield of reactions. For all compounds, an excess of ligand to metal salts in a molar ratio of 3:1 was used.

Table 24: Amount of reagents used for synthesis of ECCs based on 1,2-ethylenediamine and yields achieved.

Metal salt	**Amount of reagent**			**Yield [%]**
	Metal salt	**Ligand**	**H_2O**	
$Fe(NO_3)_3 \cdot 9\,H_2O$	0.96 g (2.39 mmol)	0.48 g (7.11 mmol)	23.7 cm^3	75
$Ni(NO_3)_2 \cdot 6\,H_2O$	0.80 g (2.76 mmol)	0.55 g (8.27 mmol)	27.6 cm^3	77
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	0.76 g (3.25 mmol)	0.43 g (9.75 mmol)	32.5 cm^3	76
$Zn(NO_3)_2 \cdot 6\,H_2O$	0.81 g (2.71 mmol)	0.54 g (8.12 mmol)	27.1 cm^3	61
$Fe(ClO_4)_3 \cdot xH_2O$	0.70 g (1.87 mmol)	0.38 g (5.62 mmol)	18.7 cm^3	85
$Ni(ClO_4)_2 \cdot 6\,H_2O$	0.84 g (2.29 mmol)	0.46 g (6.86 mmol)	26.1 cm^3	91
$Cu(ClO_4)_2 \cdot 6\,H_2O$	0.97 g (2.61 mmol)	0.35 g (7.84 mmol)	26.1 cm^3	90
$Zn(ClO_4)_2 \cdot 6\,H_2O$	0.84 g (2.25 mmol)	0.45 g (6.75 mmol)	22.5 cm^3	93

Table 25: Amount of reagents used for synthesis of ECCs based on 1,3-diaminopropane and yields achieved.

Metal salt	**Amount of reagent**			**Yield [%]**
	Metal salt	**Ligand**	**H_2O**	
$Fe(NO_3)_3 \cdot 9\,H_2O$	0.64 g (1.60 mmol)	0.28 g (3.19 mmol)	16.0 cm^3	79
$Ni(NO_3)_2 \cdot 6\,H_2O$	0.57 g (1.95 mmol)	0.34 g (3.90 mmol)	19.5 cm^3	82
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	0.61 g (2.63 mmol)	0.30 g (5.25 mmol)	26.3 cm^3	81
$Zn(NO_3)_2 \cdot 6\,H_2O$	0.57 g (1.92 mmol)	0.33 g (3.85 mmol)	19.2 cm^3	79
$Fe(ClO_4)_3 \cdot xH_2O$	0.63 g (1.68 mmol)	0.29 g (3.36 mmol)	16.8 cm^3	97
$Ni(ClO_4)_2 \cdot 6\,H_2O$	0.62 g (1.70 mmol)	0.30 g (3.40 mmol)	17.0 cm^3	84
$Cu(ClO_4)_2 \cdot 6\,H_2O$	0.71 g (1.93 mmol)	0.22 g (3.85 mmol)	19.3 cm^3	85
$Zn(ClO_4)_2 \cdot 6\,H_2O$	0.63 g (1.68 mmol)	0.29 g (3.36 mmol)	16.8 cm^3	82

Table 26: Amount of reagents used for synthesis of ECCs based on tris(2-aminoethyl)amine and yields achieved.

Metal salt	**Amount of reagent**			**Yield [%]**
	Metal salt	**Ligand**	**H_2O**	
$Fe(NO_3)_3 \cdot 9\,H_2O$	0.76 g (1.87 mmol)	0.58 g (3.74 mmol)	18.7 cm^3	87
$Ni(NO_3)_2 \cdot 6\,H_2O$	0.61 g (2.10 mmol)	0.66 g (4.21 mmol)	21.0 cm^3	89
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	0.61 g (2.61 mmol)	0.54 g (5.23 mmol)	26.1 cm^3	92
$Zn(NO_3)_2 \cdot 6\,H_2O$	0.62 g (2.08 mmol)	0.65 g (4.15 mmol)	20.8 cm^3	86
$Fe(ClO_4)_3 \cdot xH_2O$	0.58 g (1.55 mmol)	0.48 g (3.09 mmol)	15.5 cm^3	91
$Ni(ClO_4)_2 \cdot 6\,H_2O$	0.66 g (1.82 mmol)	0.57 g (3.64 mmol)	18.2 cm^3	90
$Cu(ClO_4)_2 \cdot 6\,H_2O$	0.81 g (2.19 mmol)	0.45 g (4.37 mmol)	21.9 cm^3	94
$Zn(ClO_4)_2 \cdot 6\,H_2O$	0.67 g (1.80 mmol)	0.56 g (3.59 mmol)	18.0 cm^3	88

Table 27: Amount of reagents used for synthesis of ECCs based on tris(3-aminopropyl)amine and yields achieved.

Metal salt	**Amount of reagent**			**Yield [%]**
	Metal salt	**Ligand**	**H_2O**	
$Fe(NO_3)_3 \cdot 9\,H_2O$	0.52 g (1.28 mmol)	0.52 g (2.56 mmol)	12.8 cm^3	95
$Ni(NO_3)_2 \cdot 6\,H_2O$	0.44 g (1.50 mmol)	0.61 g (3.00 mmol)	15.0 cm^3	86
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	0.48 g (2.07 mmol)	0.56 g (4.13 mmol)	20.7 cm^3	98
$Zn(NO_3)_2 \cdot 6\,H_2O$	0.44 g (1.48 mmol)	0.60 g (2.97 mmol)	14.8 cm^3	89
$Fe(ClO_4)_3 \cdot xH_2O$	0.50 g (1.34 mmol)	0.54 g (2.67 mmol)	13.4 cm^3	91
$Ni(ClO_4)_2 \cdot 6\,H_2O$	0.49 g (1.35 mmol)	0.55 g (2.69 mmol)	13.5 cm^3	88
$Cu(ClO_4)_2 \cdot 6\,H_2O$	0.60 g (1.61 mmol)	0.44 g (3.22 mmol)	16.1 cm^3	77
$Zn(ClO_4)_2 \cdot 6\,H_2O$	0.50 g (1.34 mmol)	0.54 g (2.67 mmol)	13.4 cm^3	91

In order to simplify the notation of the names of compounds, the corresponding sample codes were adopted, which were used further in the work.

Table 28: Sample codes corresponding to obtained energetic coordination compounds in configuration M-L-A (where M - metal; L - ligand; A - oxidizing anion; N indicates NO_3^-, C indicates ClO_4^-).

Metal	**Ligand**			
	EDA	**DP**	**TAEA**	**TAPA**
Fe	Fe-L1-N	Fe-L2-N	Fe-L3-N	Fe-L4-N
	Fe-L1-C	Fe-L2-C	Fe-L3-C	Fe-L4-C
Ni	Ni-L1-N	Ni-L2-N	Ni-L3-N	Ni-L4-N
	Ni-L1-C	Ni-L2-C	Ni-L3-C	Ni-L4-C
Cu	Cu-L1-N	Cu-L2-N	Cu-L3-N	Cu-L4-N
	Cu-L1-C	Cu-L2-C	Cu-L3-C	Cu-L4-C
Zn	Zn-L1-N	Zn-L2-N	Zn-L3-N	Zn-L4-N
	Zn-L1-C	Zn-L2-C	Zn-L3-C	Zn-L4-C

5.2. INFRARED SPECTROSCOPY

IR spectroscopic measurements were conducted using a Perkin-Elmer Spectrum Two (Waltham, MA, 36 USA) spectrometer, equipped with a universal attenuated total reflectance (UATR) (Single 37 Reflection Diamond) module. The spectra of the investigated post-synthesis compounds and raw materials (metal salts and ligands) were recorded in a spectral range of 650 – 4000 cm^{-1}.

5.3. RAMAN SPECTROSCOPY

Raman spectra were recorded using an InVia confocal Raman spectrometer from Renishaw (Great Britain) equipped with a DM2500 microscope from Leica (Germany). The excitation source was a helium-neon gas laser (514 and 633 nm). For measurements, a diffraction grating with 1200 lines/mm was used. During Raman analyses, 1 % or 5 % of the maximum laser power was used, which was 7.6 mW measured on a 50x objective. To focus on the sample surface, a 50× Leica magnifying lens was used (numerical aperture of the lens N.A. = 0.75), for which the size of the laser beam interacting with the sample is approximately 2 μm. The detector was a camera with a high-resolution CCD (Charge Coupled Device) matrix.

For safety reasons, Raman spectroscopic measurements were carried out for aqueous solutions of all tested ECCs, in the spectral range of 170 to 2000 cm^{-1}. In the case of Cu-L2-C and Cu-L3-N, solid samples of the compounds were investigated via Raman spectroscopy, in the spectral range of 120 – 3500 cm^{-1}. Measurements were carried out with an exposure time of 10 s and an accumulation number of 5. For each sample, measurements were made in at least 3 randomly selected locations of each sample. The initial analysis of the spectra was carried out using Renishaw's Wire 3.2 software.

5.4. Scanning electron microscopy

The morphology of the obtained compounds obtained was determined using scanning electron microscope Inspect S50-FEI and Phenom with EDS detector. Measurements were carried out at an electric field voltage of 10 and 15 kV with magnification of 2000x.

5.5. X-ray diffractometry

Powder X-ray diffraction measurements of the obtained compounds were performed using a Rigaku MiniFlex 600 diffractometer using a solid-state silicon strip detector D/teX Ultra. The powder X-ray diffraction (PXRD) patterns were recorded in the doubled scattering angle range of 3 – 80 ° (2 θ) using Cu-Kα radiation (λ = 1.5406 Å) operated at 40 mA and 15 kV using Bragg–Brentano geometry with the scanning step size of 0.01°. The exposure time at each point was 1.67 seconds without the sample rotation. For all scans, the IHS slit = 5 mm, Soller slits = 2.5°, and DS slit = 1.25° was used.

5.6. Cyclic voltammetry

Cyclic voltammetry measurements were carried out using Metrohm-Autolab PGSTAT 302N and PGSTAT M101 potentiostats. Measurements were performed in a standard three-electrode electrochemical cell, comprising: platinum wire (d = 0.2 mm, l = 5 mm) as the working electrode, platinum wire coil (d = 0.2 mm, ϕ = 5 mm, 10 loops) as the counter electrode and silver wire (d = 0.2 mm) as the pseudoreference electrode (Fig. 40).

The supporting electrolyte solution used for all presented electrochemical measurements was 0.1 M tetrabutylammonium tetrafluoroborate in N,N-dimethylformamide. Experimental solutions were produced by dissolving the tested ECCs in this supporting electrolyte, to achieve a ECCs concentration of 10 mg/ml. The electrochemical cell was purged for 15 min with an inert gas (Argon, 5N purity) and an inert gas flow was maintained over the experimental solution surface during all measurements.

Electrochemical investigations were conducted via cyclic voltammetry, at a standard potential scanning rate of 0.1 V/s. The pseudoreference electrode potential was calibrated against the ferrocene/ferrocenium (Fc/Fc+) redox couple prior to and after each measurement, with the potentials applied to the working electrode being reported vs. Fc/Fc+.

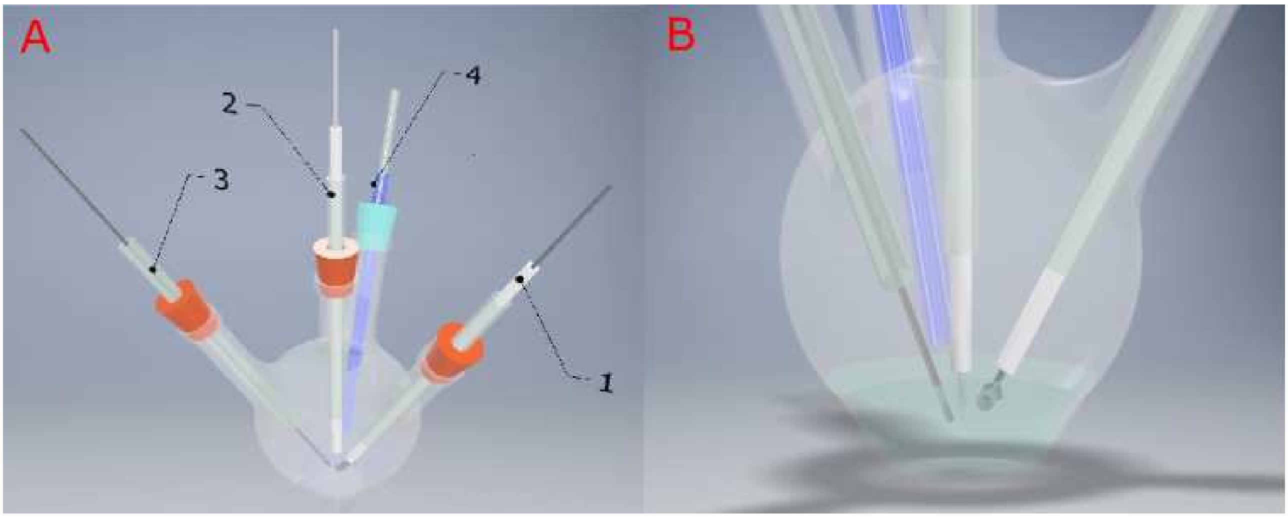


Figure 40: Scheme of equipment used for electrochemical investigations.

Where: 1 - counter electrode; 2 - pseudoreference electrode; 3 - working electrode; 4 - gas insertion tube

5.7. Investigation of the sensitivity to friction and impact

The friction and impact sensitivity values of the obtained compounds were determined in accordance with international standards EN 13631-3:2005 [211] using a Peters friction apparatus and EN 13631-4:2002 [212] using a BAM fallhammer, respectively.

As a result of the friction sensitivity test, the values of the upper limit of insensitivity were determined, i.e. such values of the maximum load that do not cause a reaction in the tested material at 6 trials. Determination of impact sensitivity values involved determining the upper limit of insensitivity, i.e. the lowest impact energy of the hammer at which no reaction was observed to occur in six trials.

5.8. Thermochemical studies

The ignition/explosion temperatures of the obtained energetic coordination compounds were determined using an Automatic Explosion Temperature Tester - AET 402 (OZM Research, Bliznovice, Czech Republic) operating over a temperature range of 100 to 400 °C. This technique was the fundamental technique for performing thermochemical studies.

The AET 402 apparatus is composed of a heating block with 6 holes filled with a small amount of Rose metal to ensure adequate heat transfer. The stainless-steel heating block is surrounded by an isothermal jacket filled with water, providing protection of the device's enclosure from excessive heat released during the measurement, as well as providing cooling of the heating block after the completion of the measurement. The apparatus is equipped with 5 independent pieces of explosion sensors. Measurement of the ignition/explosion temperature is based on placing a given amount of explosive in the test tube (50 mg for initiating explosives, 200 mg for secondary explosives), placing the test tubes in the heating block and then positioning the explosion sensors at an appropriate distance above the sample (from 0.5 to 1 cm, depending on the amount of material in the test tube). This makes it possible to perform 5 independent measurements simultaneously. The measurement can be carried out at a constant heating rate in the range of 0.1 to 20.0 °C, or it is possible to determine at a given temperature the time to explosion in isothermal mode. The apparatus is equipped with an automatic data acquisition unit, which registered on the computer continuously (using ADET software for data acquisition and evaluation).

For all ECCs, tests were conducted in the temperature range of 100 – 400 °C with a constant heating rate of 5 °C/min. The result obtained represent the average of 5 measurements and the mass of each sample was 50 ± 1 mg.

As a complementary technique, differential scanning calorimetry (DSC) analysis was carried out using a DSC 3 scanning calorimeter (Mettler-Toledo). Samples for DSC measurements were placed in standard 40 μl aluminum crucibles with a single hole in the lid. The sample was heated in the temperature range of 20 – 350 °C at a heating rate of 5 K/min under a flow of N_2. For each sample, the measurement was performed three times.

5.9. ENERGETIC PERFORMANCE OF ECCS

Energetic performance of ECCs in prototype detonators were determined in the underwater explosion test in accordance with EN 13763-15 [213]. All measurements were repeated 5 times.

In order to prepare detonators, Al-Zn alloy shells with the following dimensions were used: outer diameter 6.4 mm; wall thickness 0.7 mm; length 62.5 mm. The shells were placed inside the steel matrix, and then a dose of the pressed material was poured into the shells and pressed with a hydraulic press with a stamp, using a set force of 1100 N. During pressing, the one-sided pressing technique was used. After pressing the initiating material, an aluminium cap was placed on the material and pressed again. All components used for preparation of detonators were dried at 60 °C before the materials were placed in the Al-Zn shell. Before determining the detonation performance of the selected ECCs, reference detonators containing lead(II) azide and also PETN were tested in order to select a suitable amount for use in the prototype detonators.

Pressing the explosive material in the detonator in multiple stages, was utilised to ensure uniform density throughout the charge. In the reference detonators, 600 and 800 mg of secondary material (PETN) were used respectively, for which loading into detonators was done in two stages (300 and 400 mg by mass each). For the reference detonator containing 1000 mg of PETN, pressing was done in three stages: 400, 400 and 300 mg, respectively. In the next stage, the initiating explosive (PbN_6, 300 mg mass) was pressed in one stage, and then pressed with an aluminum cap to ensure adequate mechanical strength of the detonator. The process of detonators preparation for all prepared ECCs proceeded in the same way.

Exact data on the number of pressing operations for the reference detonators (5 detonators for each type) as well as those containing energetic coordination compounds and weights for each test batch are shown in Tab. 29. Reference detonators were prepared in a similar manner.

For the preparation of the detonators, 0.2 fuse heads produced by Nitroerg S.A. were used, which were placed inside a plastic shell and then clamped into the detonator in such a way as to ensure watertightness. PETN class 4 according to MIL-P-387 C, produced by GSS SA, and lead azide(II) class DS according to BN-90 6092-04, produced by Nitroerg S.A., were used as auxiliary explosive charges.

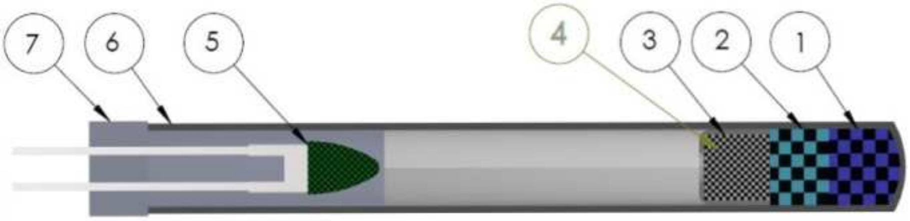


Figure 41: Schematic diagram of detonator containing ECCs where: 1 - high density ECC layer, 2 - low density ECC layer, 3 - aluminum cap, 4 - lead(II) azide layer, 5 - fuse head, 6 - Al-Zn alloy shell, 7 - rubber shield.

The water tank used to perform the tests was constructed from a stainless steel rack, the inner walls of which were lined with high-density polyurethane panels designed to absorb the energy of the explosion and avoid reflection of the shock wave (Figure 42). A positioning arrangement structure for the pressure sensor and detonator was placed at the top of the tank. The detonators used were placed vertically 550 mm below the water level (measured from the center of the detonator). For the tests, a tourmaline pressure sensor (Piezotronics 138A10 PCB, sensitivity 73.15 mV/MPa) was used, which was placed 400 mm from the detonator shell (measured from the center of the pressure sensor) and 550 mm below the water level. The distance between the detonator and the tank wall was 300 mm. Data from the sensor were recorded using an AMC VIBRO CONDITION 8000D signal conditioner and a Textronic oscilloscope. The obtained shock wave overpressure waveforms over time were analyzed using Origin software, taking into account the time interval between the peak shock wave pressure and the first collapse of the gas bubble. For both reference detonators and detonators containing ECCs, all tests were repeated 5 times. During the experiments performed, the temperature of the water in the tank ranged from 19.5 to 20 °C.

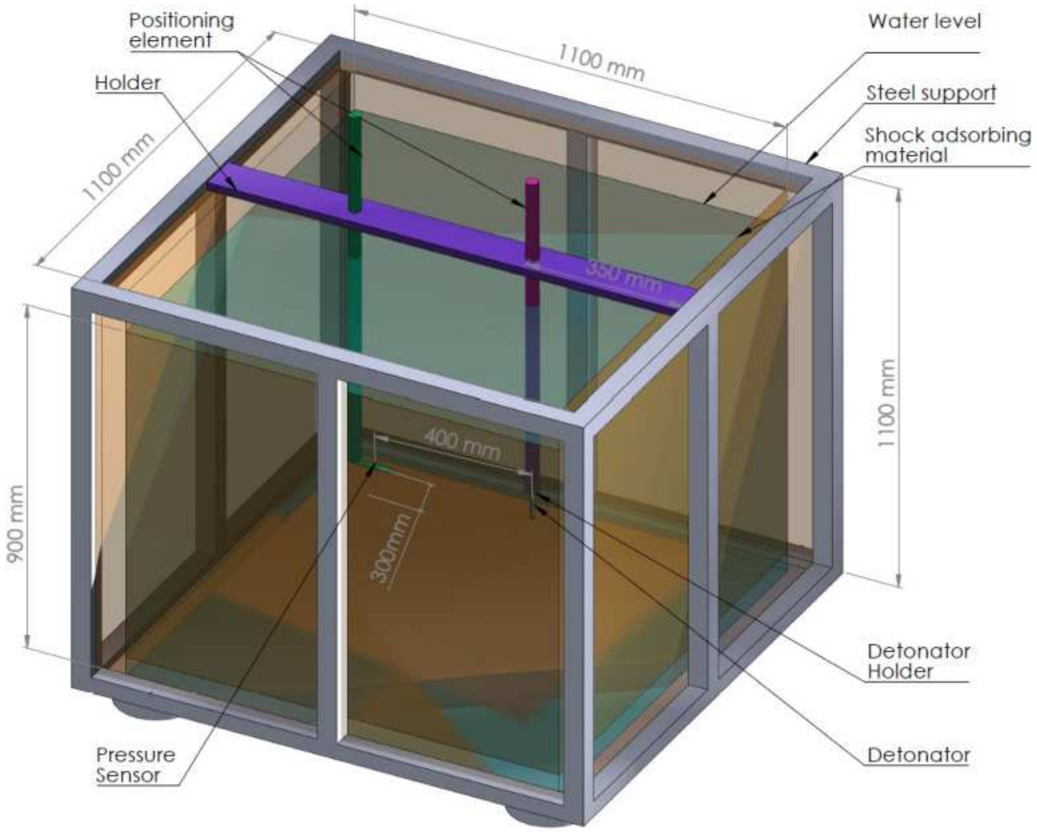


Figure 42: Schematic diagram of the water tank used for the underwater explosion test.

Table 29: Number of pressing operations for preparation of detonators.

Type	Secondary HE	Mass [mg]	Steps	Initial HE	Mass [mg]	Steps
PETN600	PETN	600	2	PbN_6	300	1
PETN800	PETN	800	2	PbN_6	300	1
PETN1000	PETN	1000	3	PbN_6	300	1

Table 30: Number of pressing operations for preparation of detonators.

Type	Secondary HE	Mass [mg]	Steps	Initial HE	Mass [mg]	Steps
Z1	Cu-L1-N	800	2	PbN_6	300	1
Z2	Cu-L1-C	800	2	PbN_6	300	1
Z3	Cu-L2-N	800	2	PbN_6	300	1
Z4	Cu-L2-C	800	2	PbN_6	300	1
Z5	Cu-L3-N	800	2	PbN_6	300	1
Z6	Cu-L3-C	800	2	PbN_6	300	1

Reference detonators containing 800 mg of PETN were selected for further testing.

Parameters describing the energetic performance, such as the primary shock wave energy (E_{SW}), shock energy equivalent (E_s), bubble gas energy (E_{BW}) and bubble gas energy equivalent (E_B) were calculated from the data recorded by the pressure sensor.

Based on the results obtained indicating the value of the generated shock wave pressure (results and discussion section), 3 types of detonators were selected to determine the initiating capability against PETN. Detonators were constructed using PETN in the amount of 800 mg as a secondary material, while selected energetic coordination compounds in the amounts of 300, 600 and 900 mg, respectively, were used as the initiating material. For each type of detonator, measurements were repeated five times. Tab. 31 summarizes the number of pressing operations.

Table 31: Number of pressing operations for preparation of detonators.

Type	Secondary HE	Mass [mg]	Steps	Initial HE	Mass [mg]	Steps
Z2-300	PETN	800	2	Cu-L1-C	300	1
Z4-300	PETN	800	2	Cu-L2-C	300	1
Z6-300	PETN	800	2	Cu-L3-C	300	1
Z2-600	PETN	800	2	Cu-L1-C	600	2
Z4-600	PETN	800	2	Cu-L2-C	600	2
Z6-600	PETN	800	2	Cu-L3-C	600	2
Z2-900	PETN	800	2	Cu-L1-C	900	3
Z4-900	PETN	800	2	Cu-L2-C	900	3
Z6-900	PETN	800	2	Cu-L3-C	900	3

6. RESULTS AND DISCUSSION

As part of the ongoing research, a number of new ECCs were obtained that have not been described in the literature so far. Therefore, once these compounds were obtained, it was necessary to confirm their chemical structure. The selection of methods that confirm the structure of compounds should allow their characterization both qualitatively and quantitatively. It was decided to choose spectroscopic techniques - infrared and Raman spectroscopy, which made it possible to indicate the presence of functional groups in the molecules of the compounds. It was also important to determine the morphology of the obtained compounds, and for this purpose the scanning electron microscopy technique was chosen and powder X-ray diffraction analysis was performed. Redox properties were also determined - for this purpose electrochemical (cyclic voltammetry), which provided information on the electrochemical processes taking place. In the context of research on new energetic materials, an important issue is the determination of basic safety parameters (friction, impact, ignition/explosion temperature). On the basis of these studies, compounds were selected that could potentially find application as initiating/secondary explosives in detonators. Hence, it was decided to conduct tests to determine their explosive performance in an underwater explosion test.

6.1. INFRARED SPECTROSCOPY

The structure of the all obtained ECCs was confirmed by IR-ATR spectroscopy and Raman spectroscopy, indicating the presence of characteristic functional groups. However, the use of this method does not allow the identification of bonds between the central atom of the compound and the ligands.

For all the compounds, spectra contain signals corresponding to deformation vibrations δ N−H in the range 1500 – 1650 cm^{-1}. Absorption bands for stretching vibrations ν N−H in the range 3200 – 3600 cm^{-1} are also visible. Moreover, there are signals corresponding to ν C−H bonds in the absorption band for stretching vibrations in the range of 2850 – 3000 cm^{-1}. For deformation vibrations of δ C−C and compounds that are nitrate analogues, signals are present at values around 1500 cm^{-1} with, in turn, for perchlorate analogues containing the EDA ligand and DP less than 1400 cm^{-1}. For compounds containing TAEA and TAPA ligands, the characteristic signals for δ C−C deformation vibrations are present at values around 1500 cm^{-1}. For all compounds containing NO_3^- anion in the structure, the signal corresponding to stretching bonds for the N−O group is present at values around 1300 cm^{-1}, respectively. In turn, for all compounds containing ClO_4^- anion in the structure, the signal corresponding to Cl−O stretching bonds is present at values around 1050 cm^{-1}.

The spectra show differences in the presence of signals for the different compounds, corresponding to of ν O−H stretching vibrations at around 1750 cm^{-1}, indicating the attachment of water to the ligand molecule. Signals from the O−H group are seen for all compounds that are nitrate analogues, except for Cu-L3-N and Zn-L3-N. It can be seen that for compounds that are perchlorate analogues, water attaches to the ligand molecules in compounds containing either iron or nickel, as well as to all compounds containing the TAPA ligand. Considering the ligand molecule, it can be seen that when a ligand with a longer carbon chain (e.g. TAPA) and more branching is used, the water molecule attaches less frequently. Almost for all compounds, the spectra show a not very broad absorption band for stretching vibrations in the range 3000 – 3500 cm^{-1}, indicating the presence of O−H bonds, originating from absorbed water.

For both nitrate and perchlorate analogues, single absorption bands are present at values around 950 cm^{-1} and above 3600 cm^{-1}, indicating the presence of adsorbed ammonia, which may have separated during drying of the compounds at the synthesis stage at 60 °C. Only in the case of compounds containing DP and NO_3 anion, this signal is visible for the Cu-containing compound. Adsorption of ammonia did not occur for the group of compounds containing TAPA ligand and NO_3 anion.

All IR-ATR spectra of the synthesised compounds, as well as tables with the given signal values are provided in the appendix.

As mentioned at the beginning, selected compounds were purified. The figure below (Fig. 43 and Fig. 44) shows a comparison of the IR-ATR spectra of the compounds before and after purification, refered as purified and unpurified.

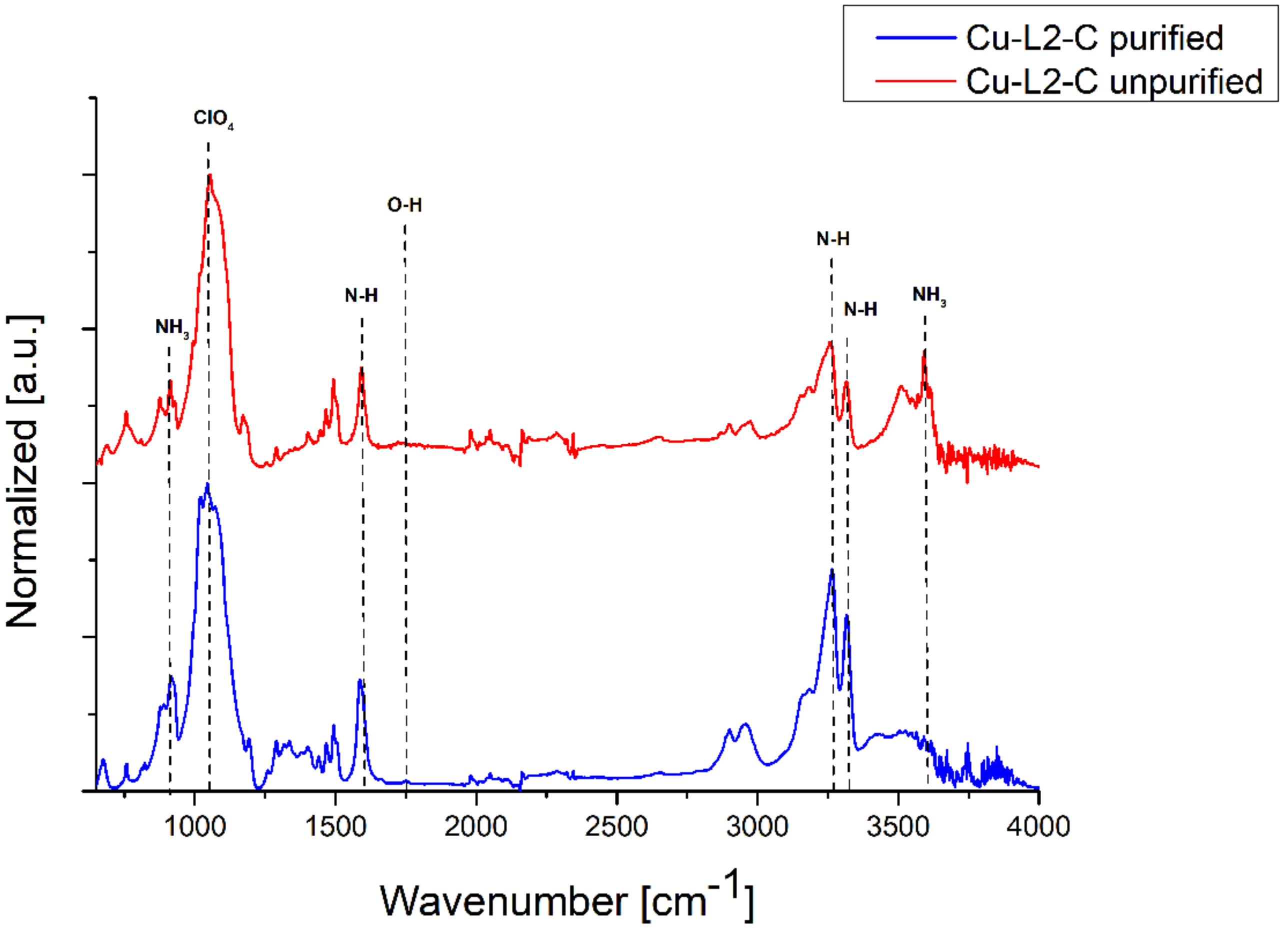


Figure 43: IR-ATR spectra for purified and unpurified Cu-L2-C.

For purified and unpurified compounds, characteristic absorption bands for N−H deformation vibrations in the 1500 – 1650 cm^{-1} (1588 cm^{-1}) range are found and absorption bands for N−H stretching vibrations in the 3200 – 3600 cm^{-1} (3266 cm^{-1} and 3316 cm^{-1}, respectively). C−H bonds are also visible in the absorption band for stretching vibrations in the range 2850-3000 cm^{-1}. For both the unpurified and purified compounds, a single absorption band for stretching vibrations is visible at 1056 cm^{-1}, indicating the presence of the overreacted ClO_4^- anion. For both samples, an absorption band for stretching vibration in the range of 3500 – 3500 cm^{-1} and an absorption band for deformation vibration in the range of 1200 – 1450 cm^{-1} are present as well, confirming the presence of a small amount of water in the samples. At values of 913 cm^{-1} and at 3592 cm^{-1} there are single peaks indicating the appearance of adsorbed ammonia in the compounds.

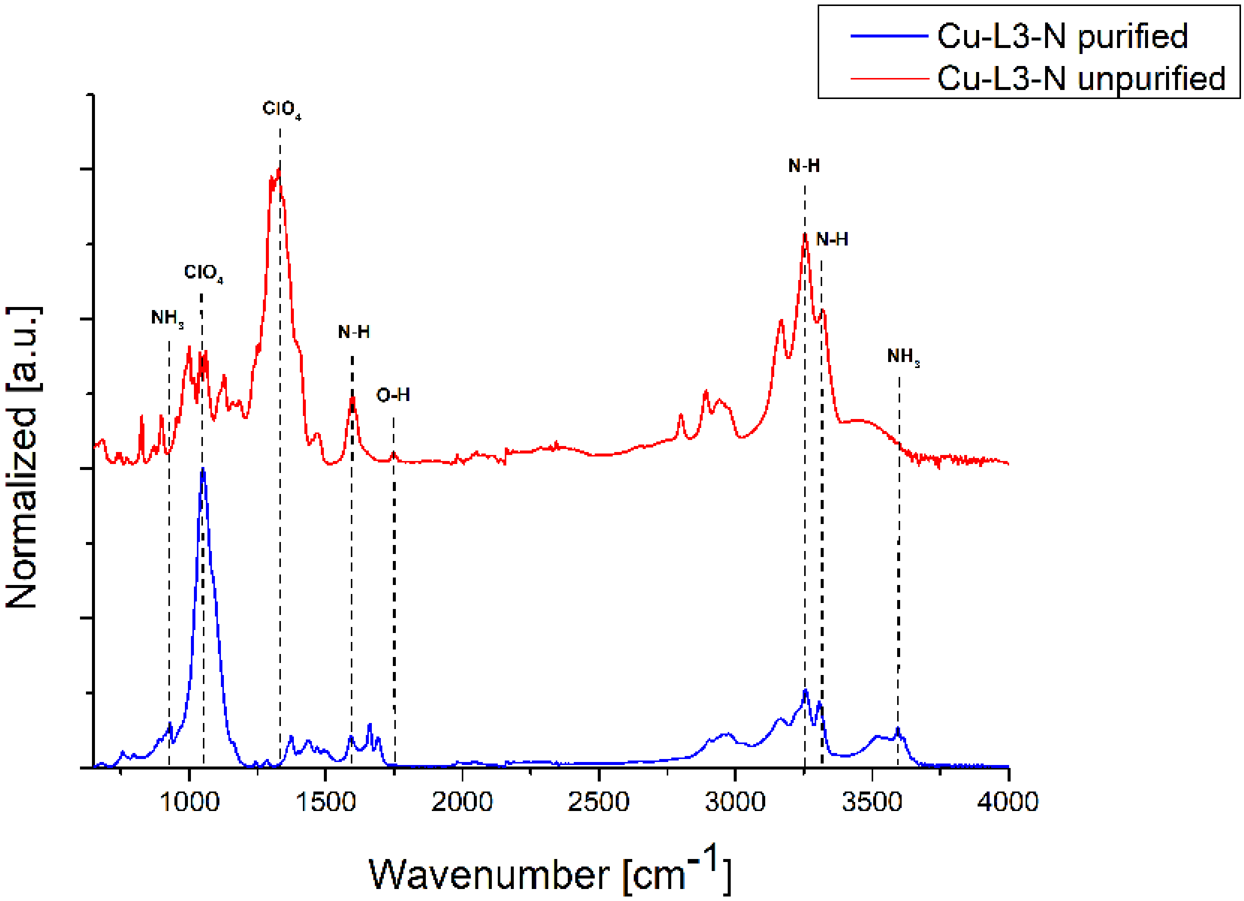


Figure 44: IR-ATR spectra for purified and unpurified Cu-L3-N.

In the case of purified and unpurified Cu-L3-N compound, characteristic absorption bands for N—H deformation vibrations are observed in the range of 1500 – 1650 cm^{-1} (1598 cm^{-1}) and absorption bands for N—H stretching vibrations are also found in the range of 3200 – 3600 cm^{-1} (3255 and 3319 cm^{-1}, respectively). C—H bonds are also present in the absorption band for stretching vibrations in the 2850 – 3000 cm^{-1} range (2893, 2950 cm^{-1}, respectively). For the unpurified sample, it is noticeable that at 1746 cm^{-1} there is a characteristic stretching vibration for the O—H bond, which indicates the attachment of a water molecule to the ligand. After purification of the sample, the water molecule is detached. In the case of an unpurified compounds, a single absorption band is visible at 1325 cm^{-1}, indicating the presence of a stretching vibration characteristic of the NO_3^- anion. For the purified sample, the characteristic signal occurs at 1060 cm^{-1}, indicating the washing out of unreacted copper nitrate during the purification process. In the unpurified sample, there is also an absorption band characteristic of the O—H bond for stretching vibrations in the range of 3000 – 3500 cm^{-1} and an absorption band for deformation vibrations of 1200 – 1450 cm^{-1}, indicating the absorption of water from the air. In addition, both a peak at 933 cm^{-1} and at 3594 cm^{-1} are visible, indicating absorption of ammonia. The purified sample has only a small amount of water. For the purified sample, signal can be seen at the value of 933 cm^{-1} and at the value of 3594 cm^{-1}, indicating the presence of adsorbed ammonia, which was released during the drying of the sample.

Based on the results obtained, it can be concluded that all compounds were successfully obtained. The spectra exhibit N−H bonds characteristic of amines and also C−H bonds. For most compounds, O−H bonds are also present, indicating the attachment of a water molecule to the ligand. The spectra also reveal signals from counterions in the form of NO_3^- and ClO_4^-, present in the compounds obtained. As a result of purification of selected compounds, the water molecule attached to the ligand was removed. It can be observed that with an increase in the chain length of the ligand and greater branching, the water molecule attached to the ligand less frequently. In the case of compounds containing a nitrate anion, the signal visible on the spectrum, characteristic of this group, is shifted from the region of the value of 1350 cm^{-1}, to the value of 1050 cm^{-1}. This indicates the leaching of part of the unreacted nitrate. For chlorate analogs, this trend does not occur.

6.2. RAMAN SPECTROSCOPY

The Raman spectra for the Cu-L2-C (Fig. 45), both for the purified and unpurified compound, contain signals corresponding to amine group (1587, 2964, 3041 cm^{-1}). In both cases, signals at 932 cm^{-1} are visible on the spectrum, indicating the presence of the ClO_4 anion. As with the IR-ATR spectra, signals are also present confirming the presence of adsorbed ammonia (814, 3271 cm^{-1}). The Raman spectrum for the Cu-L3-N compound (Fig. 46), contains signals characteristic for the amine group (1592, 2901, 2960 cm^{-1}). However, in the case of the unpurified compound, the spectrum contains a signal at 1042 cm^{-1}, indicating the presence of the unpurified ClO_4^- anion. For the purified sample, the signal for the ClO_4^- anion shifts to 932 cm^{-1}, indicating the removal of unreacted substrate. Also visible are two signals at values of 819 and 3273 cm^{-1}, indicating the presence of adsorbed ammonia.

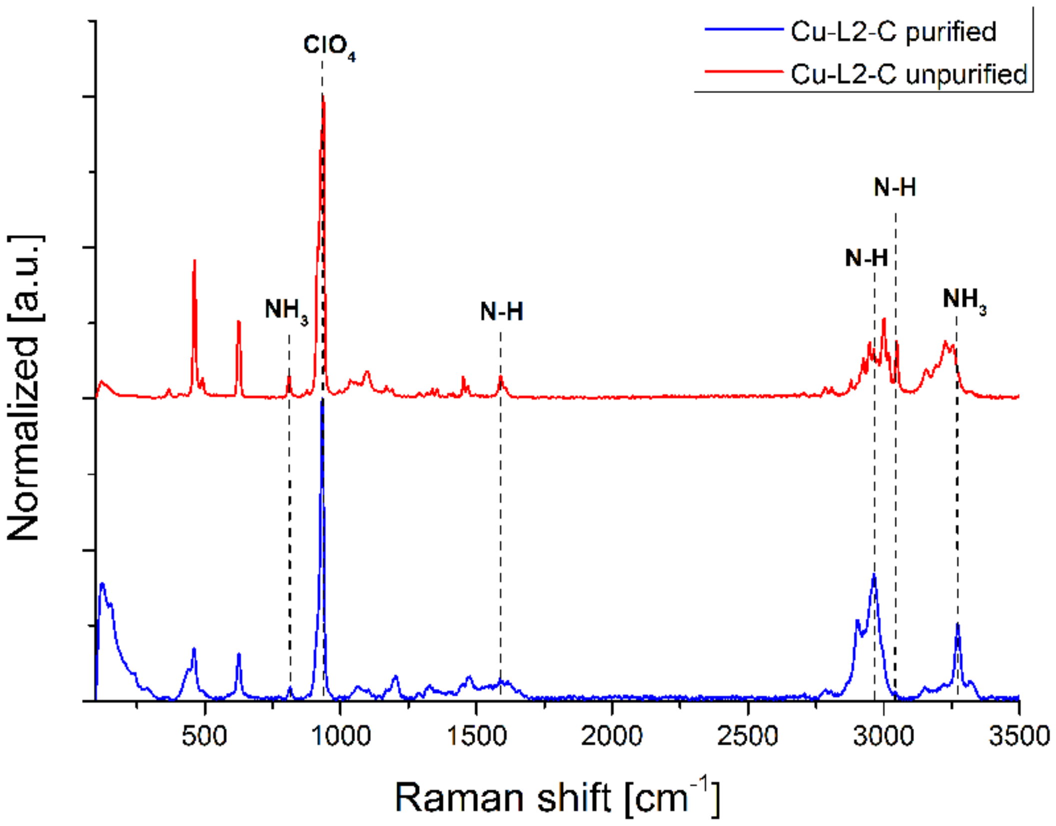


Figure 45: Raman spectra for purified and unpurified Cu-L2-C.

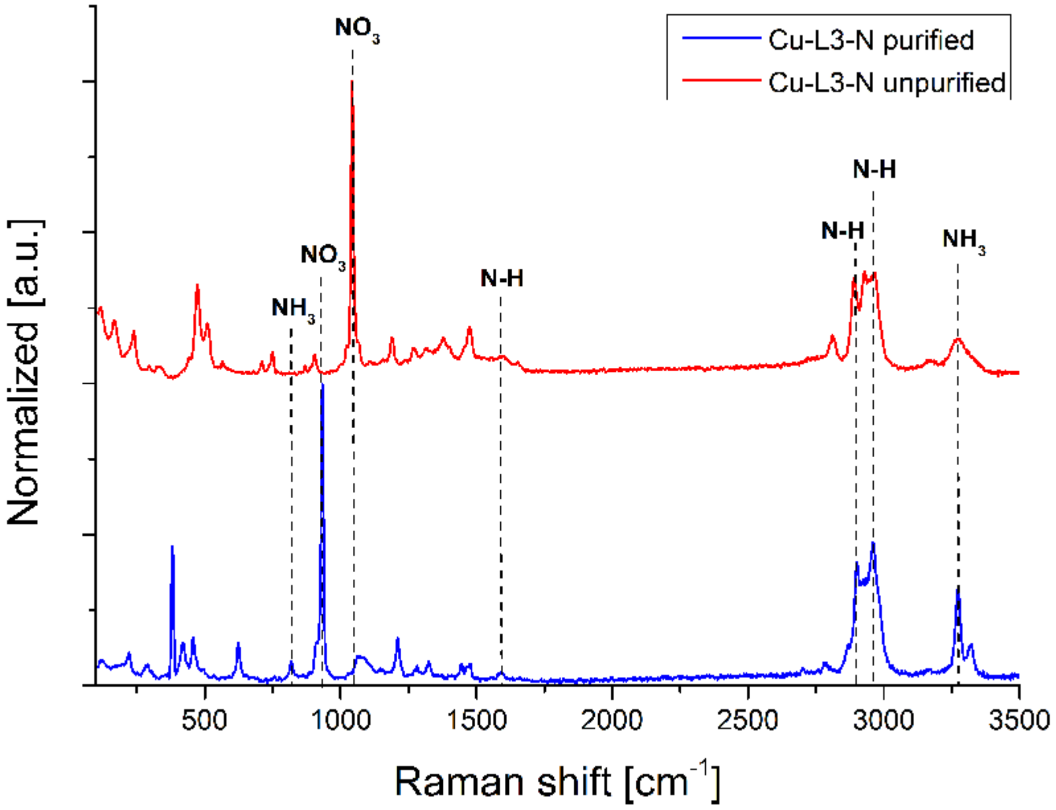


Figure 46: Raman spectra for purified and unpurified Cu-L3-N.

Raman spectra for all synthesised ECCs are provided in the appendix.

Taking into consideration all Raman spectra, they exhibit a signal corresponding to the amine group at value about 1450 cm^{-1}. For compounds containing a nitrate anion, there is a sharp signal at about 1050 cm^{-1}, confirming the presence of this anion. Compounds containing a perchlorate anion have a signal at a value of about 930 cm^{-1}, indicating the presence of a Cl$-$O bond in the compound molecule. Noticeable differences in the spectra involve the presence of a signal characteristic of the ammonia that has been adsorbed. In the case of ECCs containing 1,2-ethylenediamine (for both nitrate and perchlorate analogues), it occurs at values around 870 cm^{-1}. The exception is iron-containing compounds, for which this peak does not occur. For compounds containing 1,3-diaminopropane, ammonia is present in Ni-L2-N, Cu-2-N and all perchlorate analogues except the iron-containing compound. For compounds containing tris(2-aminoethyl)amine and the nitrate anion, ammonia was not adsorbed for the Fe-containing compound. In contrast, for perchlorate analogues, adsorption did not occur for Ni-containing ECCs. For compounds containing tris(3-aminopropyl)amine, ammonia was present only in Ni-L4-N, Fe-L4-C and in Zn-L4-C. It can be seen that for compounds containing a longer carbon chain and a higher degree of branching, less NH_3 is adsorbed.

6.3. POWDER X-RAY DIFFRACTOMETRY

In order to determine crystal structure of obtained ECCs, X-ray diffraction measurements were performed. However, determining the exact crystal structure is possible by performing a measurement from a monocrystal of a specified size, which is not always possible to obtain. Due to the varying solubility of ECCs, obtaining a monocrystal is difficult to achieve. For this reason, the test were performed for compounds in the form of fine powders (powder X-ray diffractometry).

Analyzing the diffraction patterns of both the unpurified and their purified compounds, significant differences were observed (Fig. 47 and 48). The obtained ECCs are characterised by a crystal structure, however, cannot be fully identified. The presence of only a few Cu-based phases was identified. In the case of the unpurified Cu-L2-C sample, four minority phases were identified: $Cu(ClO_4)_2 \cdot 2H_2O$ (PDF Card No. 00-032-0329), $Cu(ClO_4)_2 \cdot 4H_2O$ (PDF Card No. 01-078-2487), $Cu(ClO_4)_2 \cdot 6H_2O$ (PDF Card No. 01-079-0728) and $Cu(OH)_2 \cdot H_2O$ (PDF Card No. 00-042-0746), while for the purified compound, the two phases can coexist as secondary phases: $Cu(ClO_4)_2 \cdot 6H_2O$ (PDF Card No. 01-073-1762) and $Cu(ClO_4)_2$ (PDF Card No. 01-083-0976). For the Cu-L3-N compound, only one phase was identified for the purified sample: $Cu(NO_3)_2 \cdot 6H_2O$ (PDF Card No. 00-024-0370). Due to the amorphous nature of the ligands, their identification in the diffractograms was hindered.

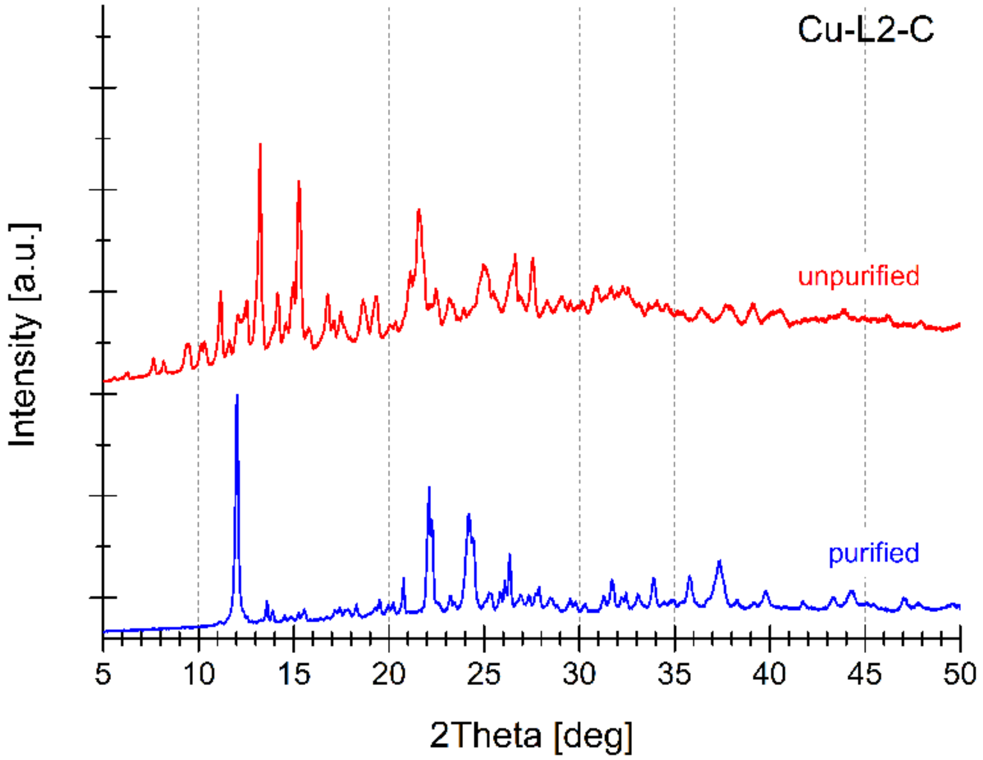


Figure 47: Powder X-ray diffraction patterns of Cu-L2-C before and after purification.

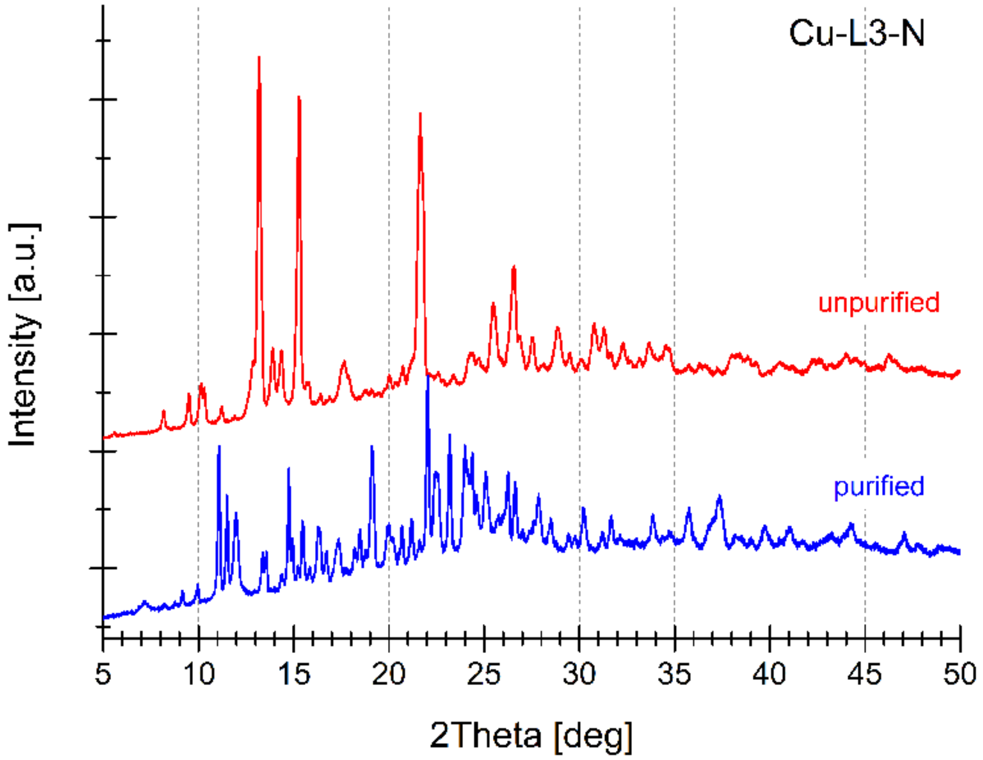


Figure 48: Powder X-ray diffraction patterns of Cu-L3-N before and after purification.

Powder XRD patterns for all obtained ECCs are provided in the appendix, as well as the diffractograms of the ligands used.

XRD diffractograms indicate that the majority of compounds can exhibit a crystalline structure, while ligands exhibit an amorphous structure. The limitation of obtaining monocrystals of compounds, in order to identify all signals on the XRD pattern, makes it difficult to indicate the crystalline arrangement. Within the work of the study performed, only the metal salts present in the compounds were indicated. On the other hand, a comparison of diffractograms of unpurified and purified compounds made it possible to indicate that the systems are multiphase. For compounds containing the ligand in the form of DP and also copper perchlorate, three copper phases are simultaneously present. For the compound containing the TAEA ligand and copper nitrate, only one copper phase was identified. It was noted that due to the greater amorphous nature of the more branched ligands (TAEA, TAPA), their identification compared to compounds with a straight chain (EDA, DP) is hindered.

6.4. SCANNING ELECTRON MICROSCOPY

For determining the microstructure of the investigated compounds, it was necessary to determine their morphology (shape and size of grains), which enabled the subsequent selection of compounds for further studies.

Analyzing the SEM images obtained for the compounds containing 1,2-ethylenediamine (Fig. 49 and 50), only in the case of the Ni-L1-N compound, a significant part of the structure is made up of needle-shaped crystals with a size of more than 30 μm, which end with sharp edges. Also present are crystals in the form of elongated polyhedrons with sharp edges. This structure of the compound indicates the presence of a crystalline or polycrystalline structure. The perchlorate analogues, containing Ni, such as Ni-L1-C, has a quite different structure, in which the particles resemble elongated polyhedrons with sharp edges and corners. In this case, it can be concluded that this compound exhibits an amorphous structure. The structure of iron-containing compounds (Fe-L1-N and Fe-L1-C) is strongly diversified, as it contains irregularly shaped and sized particles ranging from about 5 μm to particles over 30 μm in size. Compounds containing Cu and Zn have particles with irregular shape and sharp edges. All of the EDA-containing compounds do not exhibit high spatial packing.

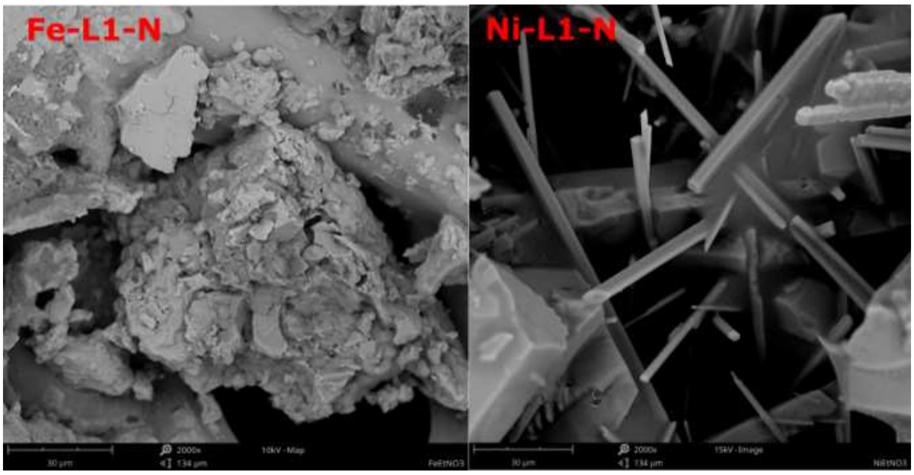


Figure 49: SEM images of ECCs containing 1,2-ethylenediamine and nitrate anion.

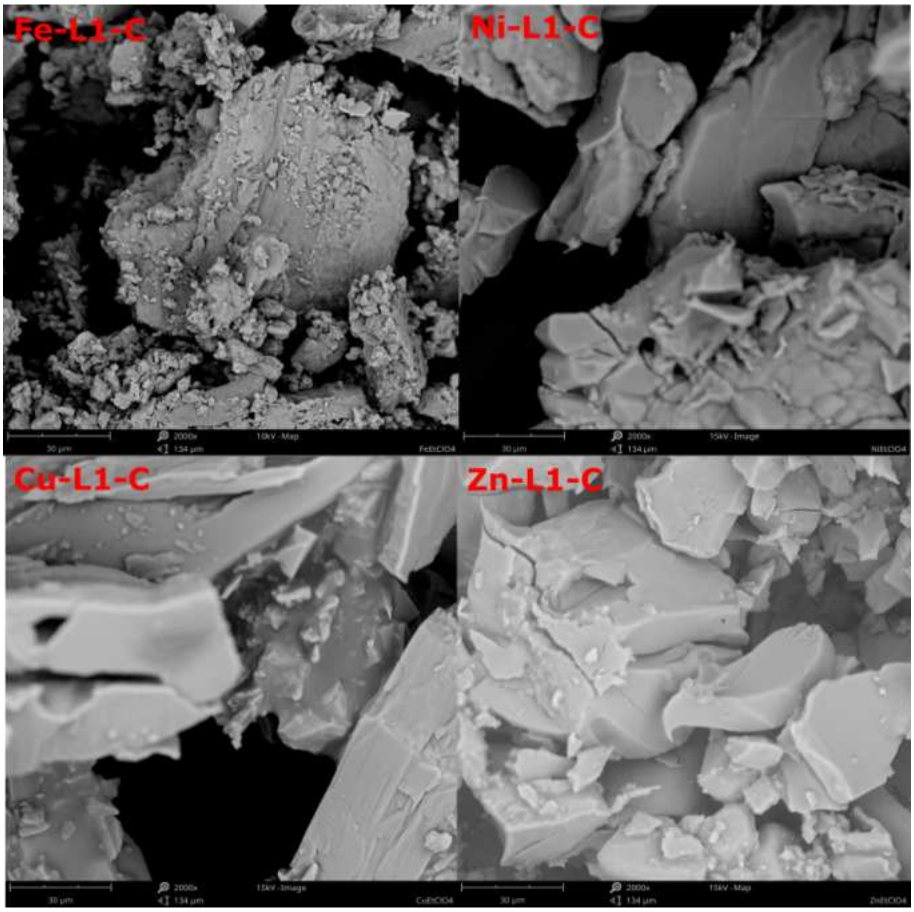


Figure 50: SEM images of ECCs containing 1,2-ethylenediamine and perchlorate anion.

Other obtained SEM images are attached in the appendix.

Compounds containing 1,3-diaminopropane, are characterised by higher spatial packing of particles. Their size is strongly diversified, however, a significant part of the structure consists of particles smaller than about 2 μm. The occurrence of crystals that are deformed cuboids, or resemble pyramids (polyhedron), indicating their polycrystalline structure, with the exception of the compound Zn-L2-C, exhibiting an amorphous structure. In the case of images of iron-containing compounds, only combustion residues can be seen, as combustion occurred when the surface was covered with a thin layer of gold.

For compounds containing tris(2-aminoethyl)amine and also tris(3-aminopropyl)amine, it can be concluded that their structure is amorphous. Copper-containing compounds (Cu-L3-N and Cu-L3-C) possess very small particles (from a size of 1 μm to about 15 μm) with irregular shapes resembling deformed polyhedrons.

Based on the obtained SEM images, it can be concluded that there is a pronounced effect of the branching of the ligand molecule on the morphology of the synthesises compounds. Compounds containing a straight chain (EDA, DP) mostly have a crystalline/polycrystalline structure, while compounds containing a branched ligand (TAEA, TAPA), on the other hand, exhibit an amorphous structure. In the context of the potential use of ECCs as initiating/secondary explosives, it is not desirable to use compounds containing needle-sized crystals (such as for the Ni-L1-C compound), as this will affect their safety parameters (higher friction and impact sensitivity). The use of iron-containing compounds is not a favorable approach, due to their instability. It may be more advantageous to use compounds with an amorphous structure and smaller particle size, as for Cu-containing compounds, hence the choice was made.

6.5. CYCLIC VOLTAMMETRY

Electrochemical investigations were carried out by cyclic voltammetry, which enabled to detrmine the redox properties (oxidation and reduction potentials) for all the ECCs obtained. During electrochemical measurements, ferrocene was used as a standard (Fc/Fc+), due to its reversible redox system), against which the obtained results were related. Before each measurement, the potential of the redox couple was determined according to the eqaution 10.

The figure below (Fig. 51) shows an example voltammogram showing the dependence of the intensity of the current flowing on the potential, for which E_0 is equal 0.45 V.

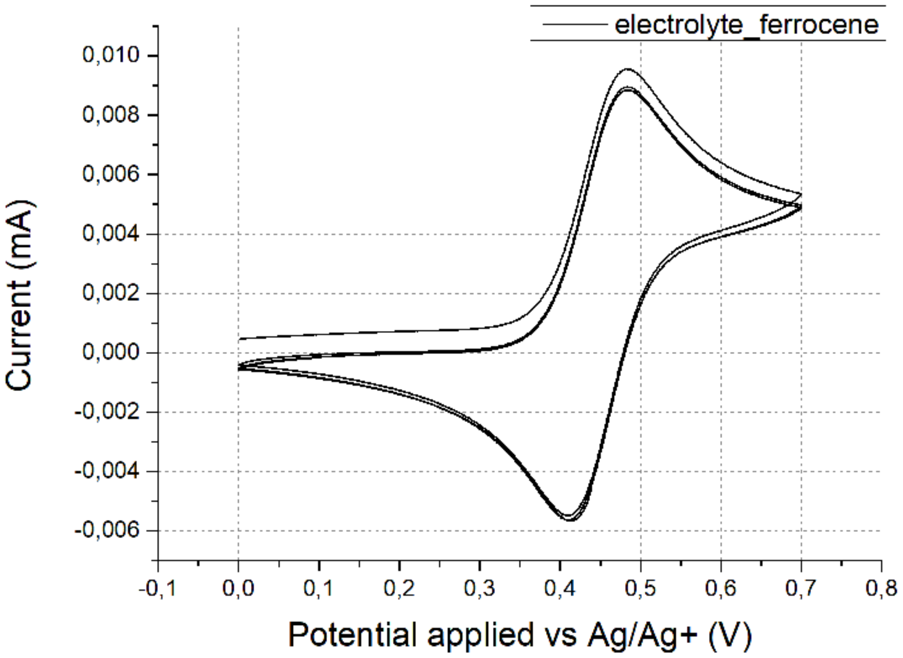


Figure 51: Voltammogram for ferrocene.

All voltamograms, together with tables indicating oxidation and reduction peak potentials, with the exception of voltamograms of ECCs containing 1,2-ethylenediamine, are attached in the appendix.

As a result of the electrode process, the Fe^{3+} as a central atom in nitrate analogues of ECCs, undergoes a single oxidation process at value -0.97 V for Fe-L2-N and 0.94 V for Fe-L4-N, with the exception of L1 and L3 ligand-containing compounds. Also for Fe-L-C containing aliphatic ligand with straight chain (EDA, DP) single reduction reaction from Fe^{3+} to Fe^{2+} are observed at values -0.74 V and -0.80 V, respectively. For perchlorate analogues containing longer and branched alkyl chain (TAEA, TAPA), oxidation reaction occurs in two stages, indicating oxidation of Fe to Fe^{2+} and from Fe^{2+} to Fe^{3+}. Moreover, Fe-based ECCs undergo reduction process from Fe^{3+} to Fe^{2+} and from Fe^{2+} to Fe. The lowest value accompanied for this process was achieved for Fe-L4-C (-2.21 V).

In contrast, for all nickel-containing ECCs, for both nitrate and perchlorate analogues there is a single process of Ni oxidation and reduction from Ni^{2+} to Ni ion, except for Ni-L3-N for which there is a three-step metal oxidation. For Cu-based ECCs, for both nitrate and perchlorate analogues, a two- or three-step oxidation and reduction of the metal are observed. In the case of the oxidation process of Zn-containing compounds, it can be seen that mostly the process takes place in two steps, with the exception of compounds containing the EDA ligand. Compounds that are perchlorate analogues have lower oxidation potentials compared to nitrate analogues. In contrast, the reduction occurs in two or three steps.

The oxidation and reduction processes taking place can be written as follows:

Oxidation:

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + 1\,e^{-}}$$
$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^{-}}$$

Reduction:

$$\mathrm{Fe^{3+} + 1\,e^{-} \longrightarrow Fe^{2+}}$$
$$\mathrm{Fe^{3+} + 3\,e^{-} \longrightarrow Fe}$$
$$\mathrm{Fe^{2+} + 1\,e^{-} \longrightarrow Fe}$$
$$\mathrm{Ni^{2+} + 2\,e^{-} \longrightarrow Fe}$$
$$\mathrm{Cu^{+} + 1\,e^{-} \longrightarrow Cu}$$
$$\mathrm{Cu^{2+} + 1\,e^{-} \longrightarrow Cu^{+}}$$
$$\mathrm{Cu^{2+} + 2\,e^{-} \longrightarrow Cu}$$
$$\mathrm{Zn^{2+} + 2\,e^{-} \longrightarrow Zn}$$

Also for Fe-L-C reduction reaction from Fe^{3+} to Fe^{2+} are observed at values.

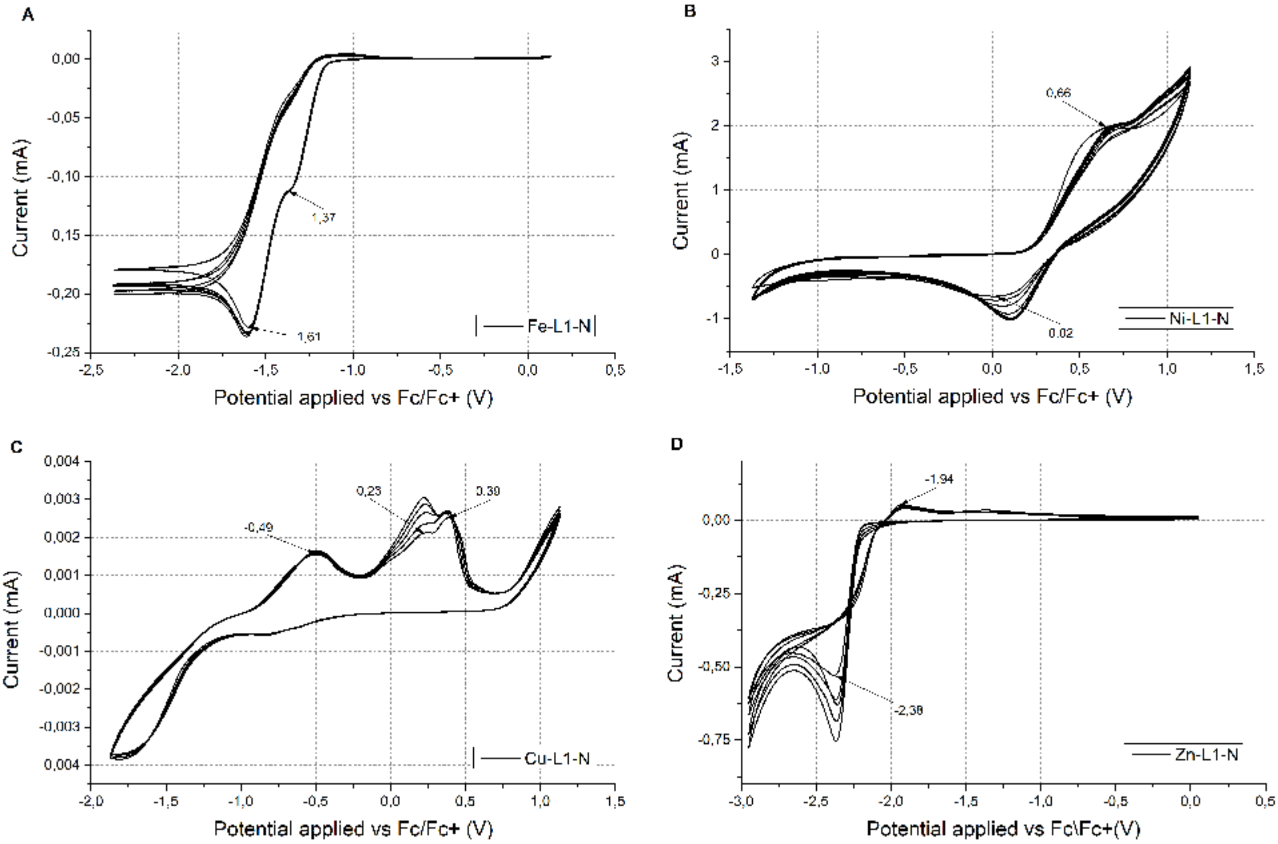


Figure 52: Voltammogram for ECCs containing 1,2-ethylenediamine and corresponding nitrate salts: A - Fe; B - Ni; C - Cu; D - Zn.

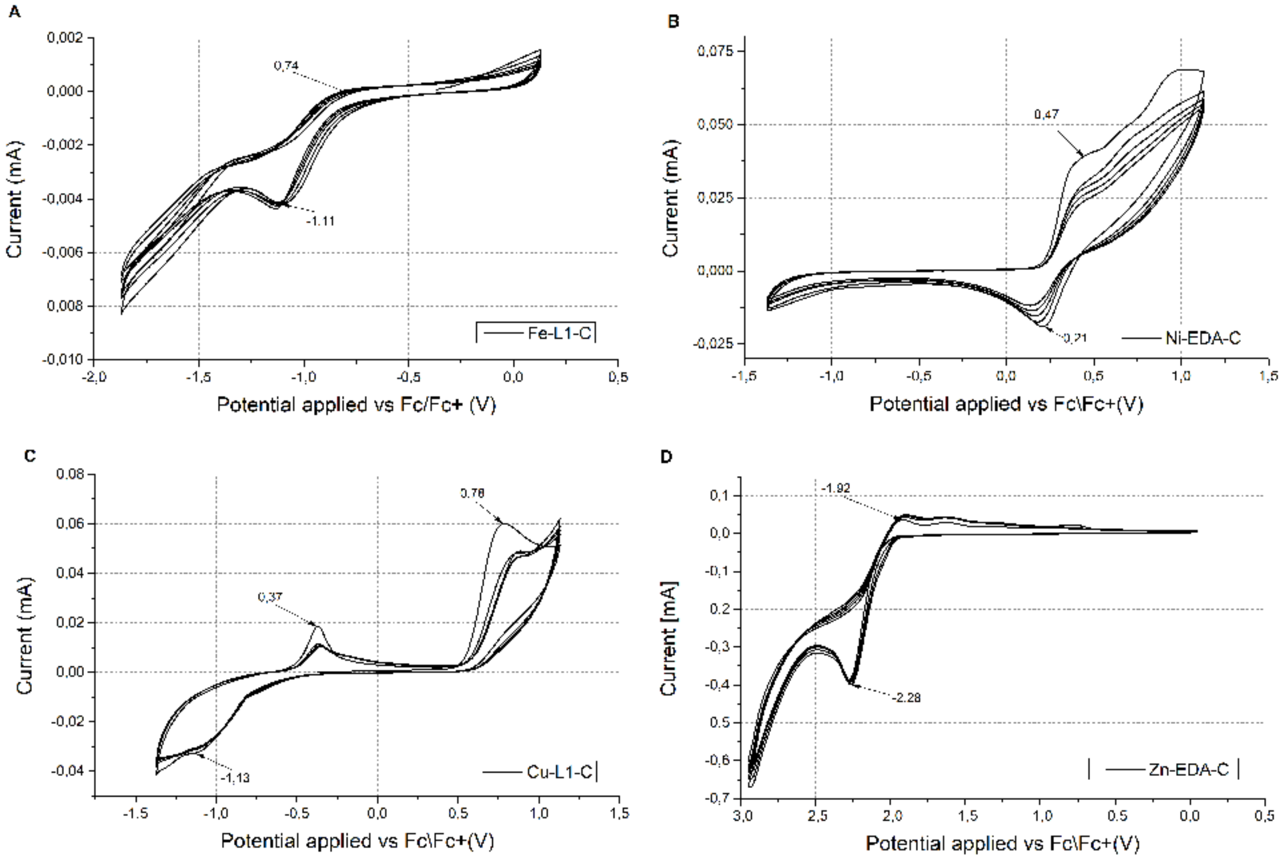


Figure 53: Voltammogram for ECCs containing 1,2-ethylenediamine and corresponding perchlorate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

Table 32: Oxidation and reduction potencial values for ECCs containing 1,2-ethylenediamine.

Sample code	Oxidation potential [V]	Reduction potential [V]
Fe-L1-N	-	- 1.61; -1.37
Ni-L1-N	+ 0.66	+ 0.02
Cu-L1-N	- 0.49; + 0.23; + 0.39	-
Zn-L1-N	- 1.94	- 2.38
Fe-L1-C	- 0.74	- 1.11
Ni-L1-C	+ 0.47	+ 0.21
Cu-L1-C	- 0.37; + 0.78	- 1.13
Zn-L1-C	- 1.92	- 2.28

It can be concluded that the electrode processes result in the oxidation and reduction of the metal present in the coordination compound, as wesll as irreversible multiple reduction of ligands included in ECCs. The literature indicates [215] that the occurrence of peaks for a given metal at different peak potential values, is related to the stability of the coordination compound and the kinetics of electron transfer. For Ni(II)-containing ECCs, the most characteristic process is the reduction from the Ni^{2+}/Ni^{+} ion [216]. In Cu(II)-containing compounds, Cu^{2+}/Cu^{+} and also Cu^{+}/Cu transitions are characteristic [217]. Due to the irreversibility of the occurring redox processes for the obtained ECCs, it can be concluded that the compounds do not exhibit stability at the electrode surface. In the case of Cu-containing compounds, the occurring copper coordination compounds in the form of Cu(I) are degraded to Cu. The authors of the paper [215] indicate that similar behaviour is exhibited by compounds with Ni(II), which may be the result of a negative charge transfer from the ligand to the metal during the formation of transition metal coordination compounds.

6.6. SENSITIVITY TO MECHANICAL STIMULI

The sensitivity of the synthesised ECCs to mechanical stimuli (impact, friction) was investigated, as these are the key safety parameters for handling energetic materials and studying them in further detail. This information was also crucial for safely producing the ECC-containing detonators investigated in this work.

Considering friction sensitivity for nitrate analogues (Fig. 54 A), the compound Fe-L4-N (60 N) is the most sensitive to friction, whereas Zn-L3-N (192 N) was the least sensitive to friction.

Compared to nitrate analogues, compounds that are perchlorate analogues are less sensitive to friction (for example for Cu-L4-C - 288 N) except for copper-containing compounds, particularly for Cu-L2-C (60 N) (Tab. 43). It is concluded, that for perchlorate compounds, a trend are observed - with the increase of alkyl chain length and degree of branching, ECCs are less sensitive to friction. This trend is not observable for ECCs containing nitrate anion.

The impact sensitivity of the ECCs is highly varied (Fig. 54 B, Tab. 44, especially for the nitrate-bearing ECCs, ranging from extremely sensitive in the case of most perchlorate-bearing ECCs, to insensitive to impact (e.g. ECCs produced using L4 and nitrate salts). Despite the lack of a clear dependence of impact sensitivity on the choice of ECC constituents, lesser correlations have been observed, such as a very similar dependence profile of impact sensitivity on the central atom for ECCs containing L2. The dependence of impact sensitivity for L3-C and L4-C ECCs on the choice of central atom was also very similar to each other. This indicates that while the changes in the constituents of the ECCs have an effect on their sensitivity to mechanical stimuli, as expected based on literature (e.g. the nitrogen content of the ECCs), this effect is not straightforward, due to the likely strong influence of the physical form (e.g. grain size and shape, degree of crystallinity) of the produced ECC samples.

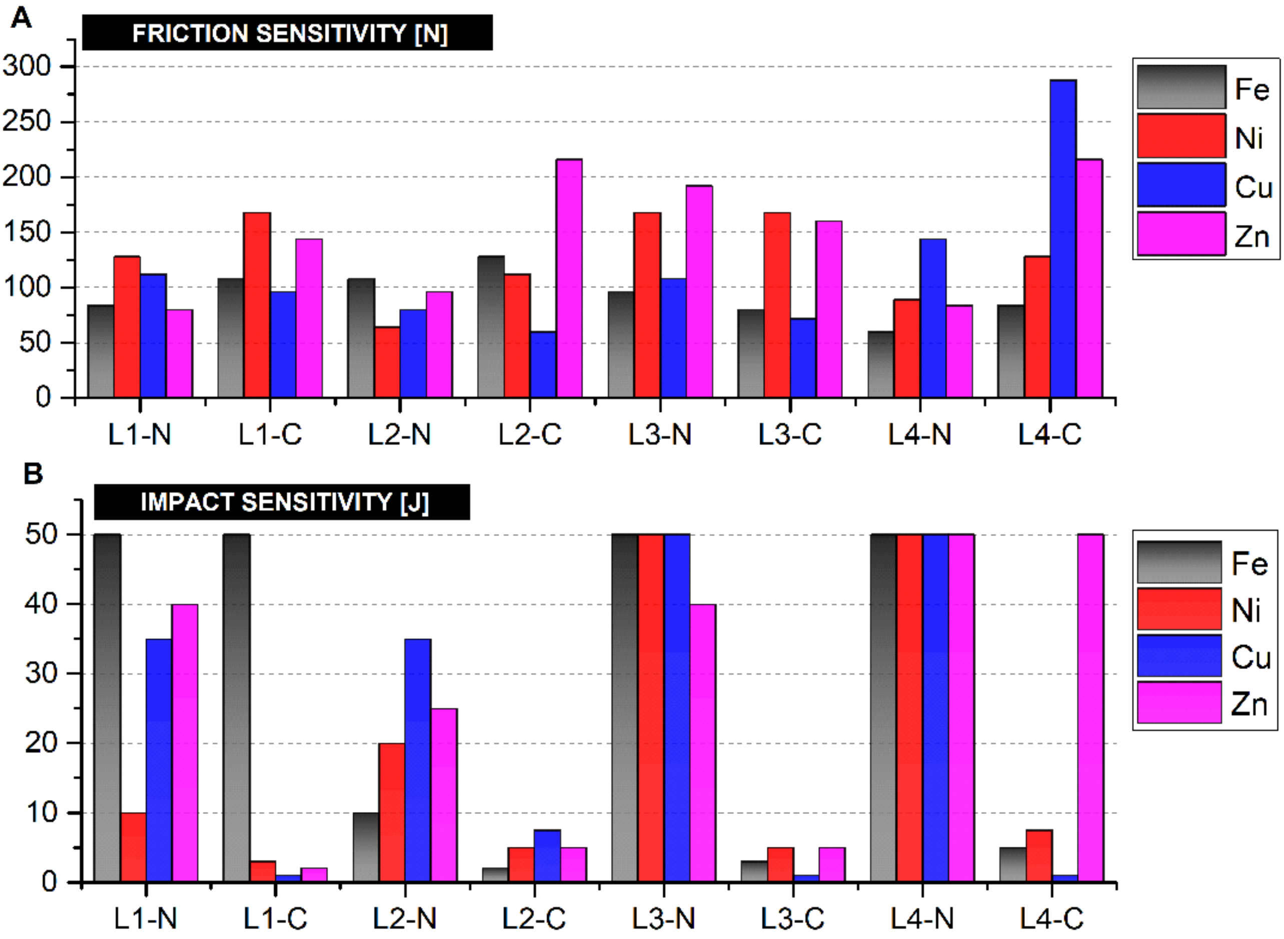


Figure 54: Sensitivity parameters for synthesises energetic coordination compounds.

The exact values of friction and impact sensitivity are shown in the tables attached in the appendix (Tab. 43 and 44).

It is noted, that in the case of friction sensitivity, all the obtained compounds are less sensitive, compared to the currently used lead(II) azide (Tab. 1), for which this value is $<$ 0.1 N. As for the impact sensitivity all ECCs are less sensitive, compared to LA for which the impact sensitivity value is $<$ 1 J. The exceptions are the Cu-L1-C and Cu-L3-C compounds (values $<$ 1 J) and the Cu-L4-C compound (1 J). These results indicate that the obtained coordination compounds containing aliphatic di- and tri-amines have better safety parameters in comparison to LA, currently used as initiating explosive.

6.7. THERMOCHEMICAL STUDIES

In addition to determining the basic safety parameters (friction, impact), it is also important to determine the ignition/explosion temperature, which determines the thermal decomposition temperature of the test compound.

Analysis of available literature shows that compounds containing perchlorate and nitrate anions undergo thermally-induced decomposition at temperatures in excess of 500 °C [218] and 330 °C [219], respectively. Conversely, the decomposition of organic ligands takes place at much lower temperatures, with ethylenediamine and its coordination compounds undergoing decomposition at approx. 300°C [220] and with coordination compounds containing propylenediamine and nitrate counter ions were found to undergo decomposition in the temperature range of 200 – 300°C [58]. As such, it would be expected for the ignition/explosion temperature (IET) of the investigated ECCs to be a function of both the choice of oxidising counter anion and the organic ligand.

IET measurements were conducted for the synthesised ECCs (Tab. 33), however, reveal that no such trend can be identified. The use of perchlorate instead of nitrate as the counter anion can both increase (e.g. for Cu-L1-N vs. Cu-L1-C) and decrease (e.g. for Cu-L2-N vs. Cu-L2-C) the observed IET of the ECCs and may have a minor (9 K for Fe-L2-N vs. Fe-L2-C) or major (122 K for Zn-L3-N vs. Zn-Le-C) impact on this parameter.

Similarly, altering the choice of utilised ligand also does not appear to have a uniform effect on the IET values of the investigated ECCs, with the transition to a longer alkyl chain leading to an increase in the IETs of the ECCs with linear ligands (L1 vs. L2), while having a mixed effect on ECCs with branched ligands (L3 vs. L4).

The choice of central atom, however, appears to have at least some discernible influence on the IETs of the investigated ECCs. In this case, iron-bearing ECCs consistently showed lower IETs than ECCs bearing other types of central atoms. This may be tentatively attributed to the redox-catalytic properties of iron cations.

Similarly, copper- and nickel-bearing ECCs typically were among the more stable thermally (high IET values). Interestingly, Zn-bearing ECCs showed extremely varied IET values (from 158°C for Zn-L3-C to 364°C for Zn-L2-C), indicating that the mechanism underlying the thermal decomposition of this group of compounds is not as straightforward as it would be expected based on literature.

Table 33: Ignition/explosion temperature for obtained ECCs. The result obtained represent the average of 5 measurements.

Sample code	**I/ET [°C]**	**Sample code**	**I/ET [°C]**
Fe-L1-N	181 ± 1	Fe-L1-C	165 ± 1
Ni-L1-N	260 ± 3	Ni-L1-C	224 ± 3
Cu-L1-N	224 ± 2	Cu-L1-C	259 ± 2
Zn-L1-N	292 ± 2	Zn-L1-C	183 ± 1
Fe-L2-N	214 ± 3	Fe-L2-C	205 ± 3
Ni-L2-N	256 ± 1	Ni-L2-C	261 ± 1
Cu-L2-N	210 ± 2	Cu-L2-C	240 ± 2
Zn-L2-N	300 ± 1	Zn-L2-C	364 ± 2
Fe-L3-N	178 ± 1	Fe-L3-C	158 ± 2
Ni-L3-N	248 ± 2	Ni-L3-C	280 ± 1
Cu-L3-N	211 ± 2	Cu-L3-C	228 ± 2
Zn-L3-N	280 ± 2	Zn-L3-C	158 ± 1
Fe-L4-N	208 ± 1	Fe-L4-C	199 ± 1
Ni-L4-N	231 ± 1	Ni-L4-C	244 ± 1
Cu-L4-N	224± 1	Cu-L4-C	233 ± 2
Zn-L4-N	253± 2	Zn-L4-C	362 ± 2

In order to better understand the processes occurring during thermally-induced decomposition of ECCs, DSC analysis was performed for selected compounds.

The thermally induced decomposition process of Cu-L2-C and Cu-L3-N occurs in two stages (Fig. 55 A). In the case of Cu-L2-C, two peaks are observed at 221 °C and 247 °C. This value coincides with the value obtained from the IET measurements. In the thermogram, the presence of the first peak indicates an earlier degradation of the compound, prior to complete degradation of the molecule, which was not observed during the IET measurements.

Thermogram for Cu-L3-N compound (Fig. 55 B) also indicate two stages of thermally induced exothermic decomposition. The first peak is observed at 237 °C and the second at 252 °C. In the thermogram, the presence of the first peak, which overlaps the second peak, indicates partial degradation of the molecule. In this case, the value for the second signal is shifted towards higher temperature and is different from the result obtained during the IET measurements. Occurrence of such difference may be caused by the measurement conditions [221], in the case of IET, test were performed in an open glass tube and for DSC in aluminium crucibles with a single hole in the lid.

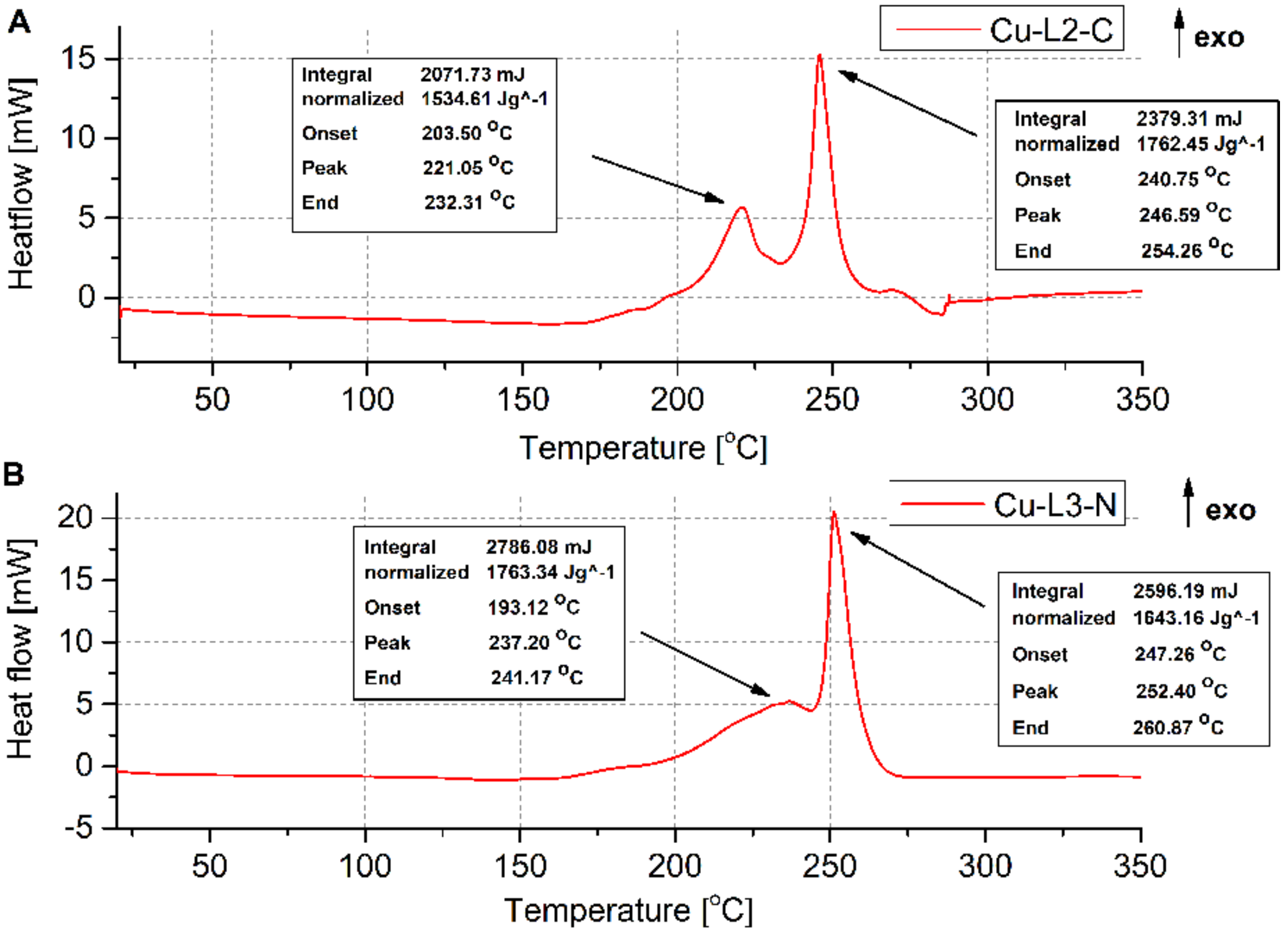


Figure 55: The DSC thermograms recorded for A) Cu-L2-C (sample mass of 1.30 mg); B) Cu-L3-N (sample mass of 1.58 mg).

Similar trends are observable for other ECCs as, for example, in the case of a compound containing nickel, 1,2-ethylenediamine as a ligand and a perchlorate anion [222]. DSC studies indicate that the compound undergoes a two separate thermal decomposition stage in the range of 205 – 270 °C. The first decomposition stage is associated with the decomposition of the ethylenediamine moiety (with an activation energy of 192 kJ/mol), while the second stage is associated with the decomposition of the perchlorate anion with the release of oxygen and consequent thermal decomposition of the whole molecule. This stage can be described by n-order kinetics with n = 1.5 with an activation energy of 351 kJ/mol. This value is characteristic of the decomposition processes of metal perchlorates.

Presumably, the occurrence of two stages of thermal decomposition will be the trend for all ECCs. In turn, on the basis of DSC studies, it was found that the tested compounds undergo thermal degradation in two stages, the first being a partial degradation of the investigated compound.

6.8. ENERGETIC PERFORMANCE OF ECCS IN PROTOTYPE DETONATORS

On the basis of preliminary studies, involving the determination of safety parameters (friction and impact sensitivity) and ignition/explosion temperatures, six ECCs were selected for studying their energetic performance.

The results of the underwater explosion test (Tab. 34) for the reference detonators indicate that the highest value of maximum pressure (P_{max} - 11.68 MPa) and total explosion energy (E - 1962.85 J) were obtained for detonators containing 1000 mg of PETN and 300 mg of lead(II) azide.

Table 34: Parameters describing the energetic performance of standard-design detonators in the underwater explosion test.

Parameter	**Amount of PETN [mg]**		
	600	**800***	**1000**
P_{max} [MPa]	9.67 ± 0.34	**10.58 ± 0.19**	11.68 ± 0.25
E [J]	1399.25 ± 16	**1696.23 ± 35**	1962.85 ± 18
t_b [ms]	21.21 ± 0.11	**22.44 ± 0.10**	23.43 ± 0.21
$E_S \cdot 10^8$ [Pa^2s]	4.63 ± 0.11	**5.77 ± 0.20**	6.80 ± 0.21
E_{SW} [J]	629.43 ± 15	**784.90 ± 27**	925.13 ± 29
$E_B \cdot 10^{-6}$ [s^3]	9.54 ± 0.13	**11.30 ± 0.16**	12.86 ± 0.34
E_{BW} [J]	769.82 ± 10	**911.33 ± 13**	1037.72 ± 28

* Standard-design detonator that was used as a reference detonator for further investigations

For ECCs containing perchlorate anion, using the same charge mass (800 mg), significantly lower overpressure was registered compared to reference detonators containing PETN. The highest recorded P_{max} value was registered for Cu-L2-C, which was 39.70 % PETN, and the lowest for Cu-L1-C was 35.07 % PETN. For nitrate analogues, the highest recorded pressure (for Cu-L3-N) was 10.30 % PETN.

For the investigated ECCs, the highest value of total explosion energy for among the LA/ECC detonators was observed for for the detonator containing Cu-L2-C (1166.63 J), which is 68.78 % of the E value for the detonator containing 800 mg PETN (Tab. 56). In this case, P_{max} was 4.20 MPa. The values obtained for the other compounds containing perchlorate anion and ligand L1 and L3 are lower. However, detonation occurred for all compounds containing a perchlorate anion.

Analyzing the parameters describing the energetic performance for nitrate analogues (t_b, E_S, E_{SW}, E_B, E_{BW} - Tab. 35), the nature of the primary shock wave generated by detonators containing Cu-L1-N, Cu-L2-N and Cu-L3-N indicates that these compounds deflagrate, therefore they are not suitable for use in detonators.

It is concluded, that the oxidizing anion has a greater influence on the energetic performance than the ligand present in the coordination compound. The selection of the anion, which in ECC should be a strong oxidant, significantly affects the heat of explosion (Q_v). According to the literature [223], for example, the heat of explosion for compounds containing the NO_3^- anion is about 700 kcal/kg, while for the ClO_4^- anion, it is about 1100 kcal/kg. Hence, it is more advantageous to use a perchlorate anion than a nitrate anion in terms of obtaining higher detonation performance.

Table 35: Parameters describing the energetic performance of ECC-based detonators in the underwater explosion test.

Parameter	**Sample code**[*]				
	Cu-L1-C	**Cu-L2-N**	**Cu-L2-C**	**Cu-L3-N**	**Cu-L3-C**
P_{max} [MPa]	3.71 ± 0.02	1.06 ± 0.07	4.20 ± 0.08	1.09 ± 0.06	3.75 ± 0.04
E [J]	1078 ± 17	188 ± 5	1167 ± 19	194 ± 5	1117 ± 8
t_b [ms]	20.86 ± 0.04	12.71 ± 0.13	21.16 ± 0.15	12.87 ± 0.15	21.51 ± 0.04
$E_S \cdot 10^8$ [$Pa^2 s$]	2.54 ± 0.04	0.16 ± 0.02	2.95 ± 0.06	0.16 ± 0.02	2.31 ± 0.05
E_{SW} [J]	345 ± 5	22.32 ± 0.30	402 ± 9	21.73 ± 0.27	314 ± 7
$E_B \cdot 10^{-6}$ [s^3]	9.08 ± 0.19	-	9.48 ± 0.20	-	9.95 ± 0.06
E_{BW} [J]	733 ± 15	166 ± 5	765 ± 16	172 ± 5	803 ± 5

[*] All detonators contain 800 mg of ECC and 300 mg of LA

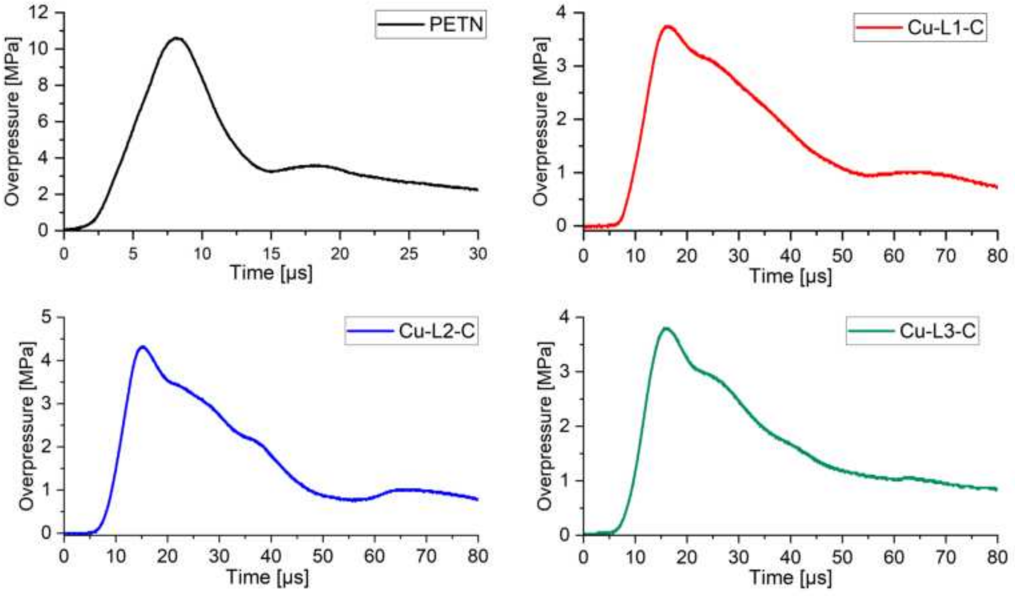


Figure 56: The primary shock wave generated in water by firing detonators filled with 800 mg of investigated explosives.

On the basis of the oscilloscope-recorded graph of the change in overpressure versus time (Fig. 57 A, B), as well as the analysis of fragments of detonator residues (Fig. 57 C, D), it was possible to determine if the ECCs undergo deflagration or detonation. For example, for the Cu-L3-N, a shorter gas bubble rise time of 12.87 ms was recorded for the deflagration process, and the gas bubble energy was 172 J. The picture of the fragments shows that for half of the Al-Zn shells, the deflagration process resulted in the complete destruction of the shell, whereas for part of it, only the tearing of a shell fragment is visible. On the other hand, for the detonation process for the Cu-L3-C, in the graph of the change in overpressure versus time, the rise time of the gas bubble is longer at 21.51 ms and the energy of the gas bubble is 803 J. This value is close to that of the reference detonator containing 800 mg PETN and is 911 J. Moreover, in the graph, a sharper signal of the pressure change is visible, indicating the release of more energy as a result of the energy decomposition of the compound. This is also confirmed by pictures of detonator fragments, indicating that most of the shells have been ruptured.

For determining energetic performance in underwater explosion test, an important parameter is the gas bubble energy [214], which is determined by the period of the gas bubble pulse, indicating the amount of energy released by the detonation of the material underwater. Considering the collapse time of the first gas bubble (t_b) (Fig. 56), the highest values were achieved for the reference detonator (22.44 ms). For nitrate analogues, these values differ by about 43 %, while for perchlorate analogues the difference is about 7 %.

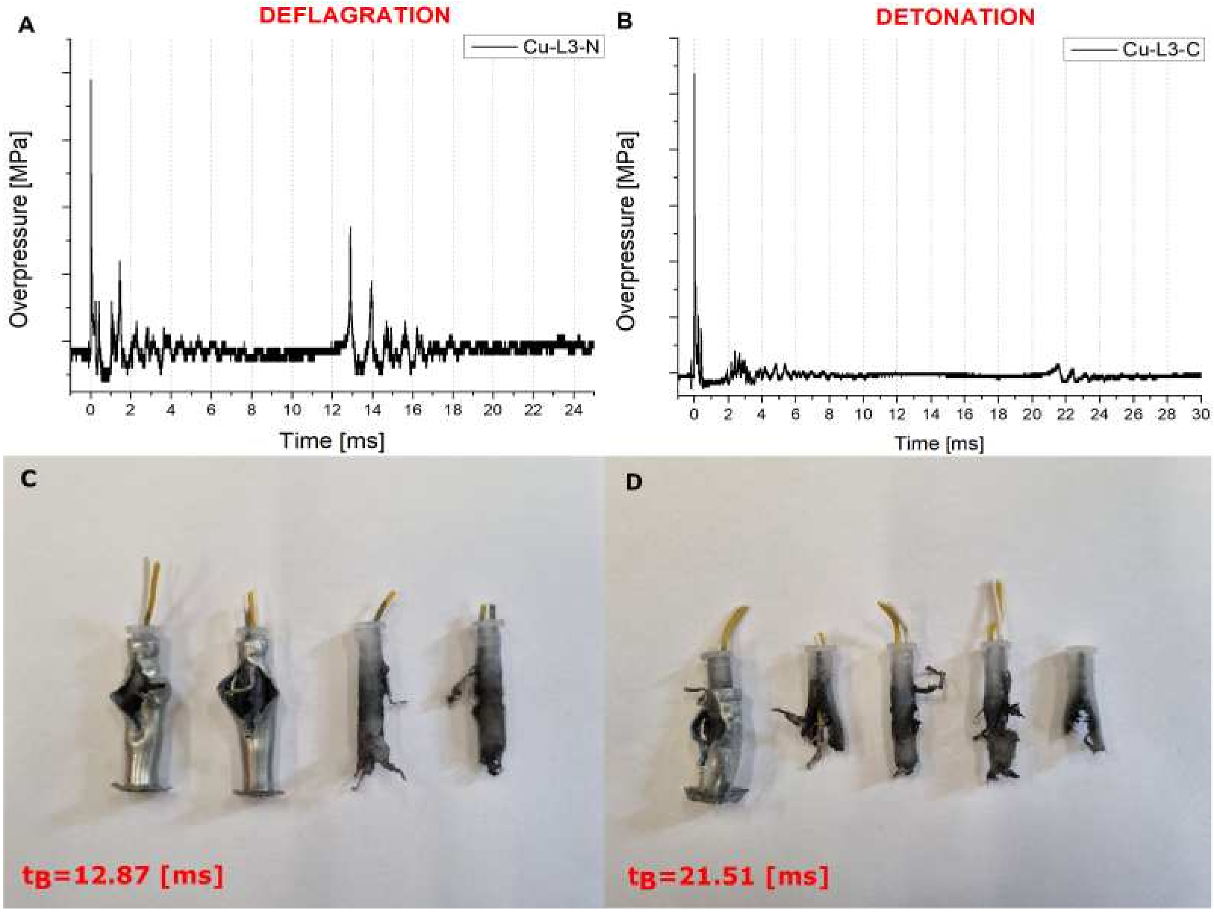


Figure 57: Schock wave-time dependence recorded after initiation of a detonator containing 800 mg of Cu-L2-N (**A**) and Cu-L3-C (**B**) indicating the occurrence of deflagration or detonation and detonator fragments.

The following photos show the remains of detonator parts that have deflagrated or detonated.

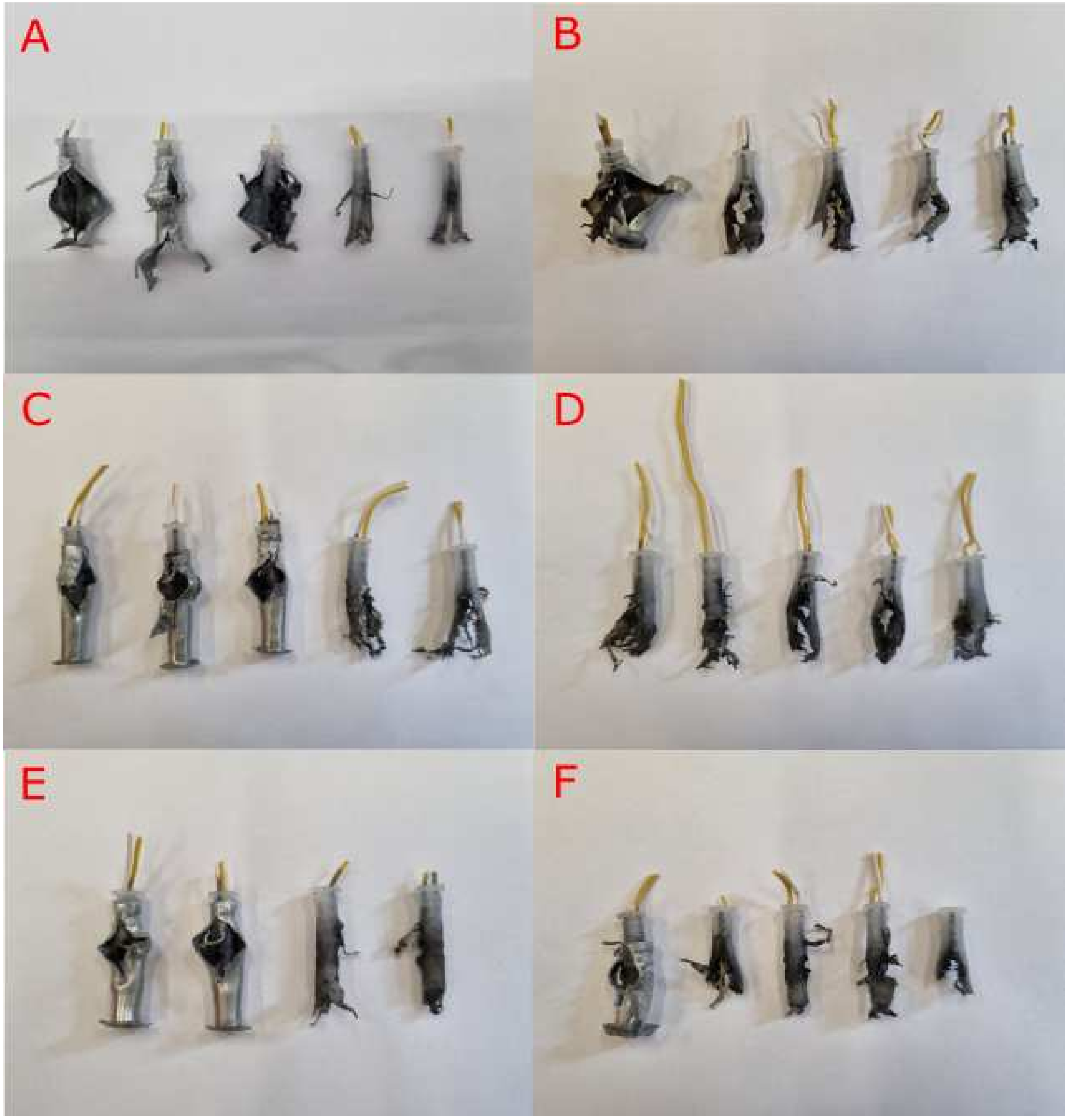


Figure 58: Detonator parts remaining after underwater explosion testing. The detonators contained ECCs in the form of: **A** - Cu-L1-N; **B** - Cu-L1-C; **C** - Cu-L2-N; **D** - Cu-L2-C; **E** - Cu-L3-N; **F** Cu-L3-C
.

Initiating capability

For selected ECCs, underwater explosion tests were performed to determine their detonation performance. The detonators tested contained LA as the initiating explosives, and ECCs as the secondary explosives in exchange for PETN. The results obtained indicated that compounds containing the nitrate anion undergo deflagration, while ECCs containing the perchlorate anion undergo detonation. The best detonation characteristics were obtained for the compound Cu-

L2-C, for which the maximum explosion pressure (P_{max}) was 4.20 MPa and the total explosion energy was 1167 J. These values represent, respectively, 39.70 % of P_{max} and 68.78 % of the E value recorded for a detonator containing 800 mg PETN. Relative to the reference detonator, the values obtained are satisfactory.

Comparing the obtained values (P_{max}, E) for detonators containing ECCs, a clear effect of the counter ion used on the detonation performance can be seen. The use of perchlorate anion, allowed the occurrence of detonation in all compounds. In addition, a slight trend can be observed regarding the use of a given ligand, indicating that as the length of the alkyl chain increases and the branching increases, higher P_{max} and E values can be obtained. Due to the form of ECCs containing the tris(3-aminopropyl)amine ligand ("gel-like" materials) and, consequently, the possible difficulties associated with pressing this compound in detonators, it was not decided to prepare detonators of this type.

On the basis of the satisfactory results for detonators containing LA/ECC, the next step was to prepare a series of detonators containing 800 mg of PETN as secondary explosive and 300, 600 or 900 mg of ECCs such as Cu-L1-C, Cu-L2-C and Cu-L3-C as initiating explosive.

Initially, detonators containing 300 mg of the ECC were tested, but no detonation was observed for any of the tested compounds. In the next step, the ECC charge was increased to 600 mg and consequently, the ECC charge was increased further to 900 mg. However, in all cases no detonation was observed, despite the increased of ECC charge.

Investigations of the initiating ability of ECC as a replacement of LA, despite the use of varied mass of the coordination compounds charge (300, 600 and 900 mg), made it possible to indicate that for these compounds only deflagration occurs. In view of this, investigated ECCs can be classified as secondary explosives rather than initiating explosives. Accordingly, these compounds are recommended for use in detonators as secondary explosives, which are able to replace PETN.

7. SUMMARY

Within the work, 32 energetic coordination compounds containing nitrate and perchlorate anions of transition metals (copper, zinc, nickel and iron) were synthesised with 1,2-ethylenediamine, 1,3-propylenediamine, tris-(2-aminoethyl)amine and tris-(3-aminopropyl)amine as an aliphatic ligands. Within the work, the analysis of the obtained results allows the statement that:

1. The structure of all obtained ECCs was confirmed by IR-ATR spectroscopy and Raman spectroscopy, indicating the presence of functional groups. On all spectra, there are characteristic signals corresponding to stretching and deformation N−H bonds and also C−H bonds. There are also signals coming from the counter ions (NO_3^- and ClO_4^-). For most compounds, O−H bonds are also present, indicating the attachment of a water molecule to the ligand. For selected compounds, as a result of purification, the water molecule was removed. In the case of ECCs containing a nitrate anion, the signal visible on the spectrum, characteristic of this group, is shifted from the region of the value of 1350 cm^{-1}, to the value of 1050 cm^{-1}. This indicates the removal of unreacted nitrate. For perchlorate analogues, this trend does not occur.

2. Through X-ray diffraction measurements, the crystal structure of ECCs were partially determined. Determining the exact crystal structure was not possible, due to the need to perform tests from a monocrystal of a specified size. Due to the varying solubility of ECCs, consequently obtaining a monocrystal is difficult to achieve. For this reason, the test for all obtained ECCs were performed for fine powders (powder XRD). Obtained diffractograms indicate that the majority of compounds can exhibit a crystalline structure, while ligands exhibit an amorphous structure.

   The limitation of obtaining monocrystals of compounds, in order to identify all signals on the XRD pattern, makes it difficult to indicate the crystalline arrangement. Within the work of the study performed, only the metal salts present in the compounds were indicated. Comparing the diffractograms of unpurified and purified compounds made it possible to indicate that the systems are multiphase. It can be seen, that due to the greater amorphous nature of the more branched ligands (TAEA, TAPA), their identification compared to compounds with a straight chain (EDA, DP) is hindered.

3. Based on the obtained SEM images for ECCs, it can be concluded that there is a pronounced effect of the branching of the ligand molecule on the morphology of the compounds. Compounds containing a straight chain (EDA, DP) mostly have a crys-

talline/polycrystalline structure. For compounds containing a branched ligand, an amorphous structure is visible.

4. Considering the application of ECCs in detonators and the associated operation of pressing materials for detonators, for all compounds friction and impact sensitivity were determined. Considering the increasing length of the alkyl chain and its degree of branching, there is a slight effect on sensitivity parameters - a reduction in sensitivity to friction and impact.

5. Detonation parameters (P_{max}, E) for selected copper-containing ECCs were determined in an underwater explosion test. The results were related to reference detonators containing 800 mg PETN and 300 mg LA. For ECCs containing perchlorate anion, detonation transformation occurred, while for compounds containing nitrate anion, deflagration occurred. The highest value of total explosion energy (1166.63 J) and maximum pressure (4.20 MPa) was achieved for the detonator containing Cu-L2-C. Consequently, this compound was selected for testing the initiating capability against PETN. As a result, the compound deflagrated and did not fully initiate PETN. Based on this, it can be concluded that the compounds tested in the underwater explosion test, in particular perchlorate analogues, show the ability to be used as secondary explosives that can replace PETN, while they cannot be used as initiators.

6. Taking into account the potential increase in the scale of production, reducing the number of synthesis steps (no purification step) is an advantage due to the reduction of production costs, production time, while maintaining greater occupational safety.

8. CONCLUSIONS

The main thesis of the research was the synthesis of new, energetic coordination compounds containing aliphatic amines as ligands, as well as the application of selected ECCs in the form of secondary explosives as substitutes for PETNs in detonators. In order to select the compounds, it was decided to perform underwater explosion tests to determine their detonation characteristics. For this purpose, it was necessary to carry out preliminary tests to determine the safety parameters of the compounds obtained. However, the chemical structure of the synthesised compounds had to be confirmed first. Compounds were obtained using synthesis in the "one-pot" solution regime. Infrared spectroscopy (IR-ATR) and Raman spectroscopy investigations confirmed that the obtained compounds contain amine groups in the structure, or -C-H bonds occurring in the alkyl chain. Moreover, for most compounds, on spectras, there was visible signal corresponding to water, which was attached to the ligand molecule. In turn, the presence of water in the molecule can affect the safety parameters (friction, impact), reducing the sensitivity of compounds to mechanical stimuli (as in the case of PETN), but at the same time affecting the worsening of detonation performance. However, in the context of the research being carried out and the assumption arising from the synthesis of compounds involving as few as possible synthesis steps and their purification, as well as keeping production costs as low as possible, it was decided to obtain detonators from ECCs that can contain a small amount of coordinated water.

Investigations of the safety parameters of all the ECCs obtained indicated that the compounds exhibit lower friction and impact sensitivity compared to lead(II) azide. Compared to PETN, for which the friction sensitivity is 50 N and the impact sensitivity is 3.5 J, the ECCs showed lower friction sensitivity and comparable impact sensitivity, and in some cases they were not sensitive to impact. Considering the flash point of the obtained ECCs, all compounds had high thermal stability and thermally decomposed above 200 °C, with the exception of most Fe-containing compounds. DSC analysis indicated that the ECCs undergo exothermic two-step decomposition, in which, according to the literature, in the first step there is partial degradation of the molecule and in the second step there is a complete decomposition of the compound. Based on friction, impact and flashpoint sensitivity studies, compounds were selected and investigated for their detonation performance. The best performance was achieved for the compound Cu-L2-C, for which the total detonation energy was 68.78 % of that of a detonator containing 800 mg PETN and the maximum detonation pressure 39.70 % of the P_{max} value for PETN.

Accordingly, the hypothesis assumed within the thesis was confirmed and the results obtained allowed the selection of ECC, from which the best detonation performance was achived for Cu-L2-C, which can be an alternative as a replacement for PETN in detonators.

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9. BIBLIOGRAPHY

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A. Appendix

Infrared spectroscopy

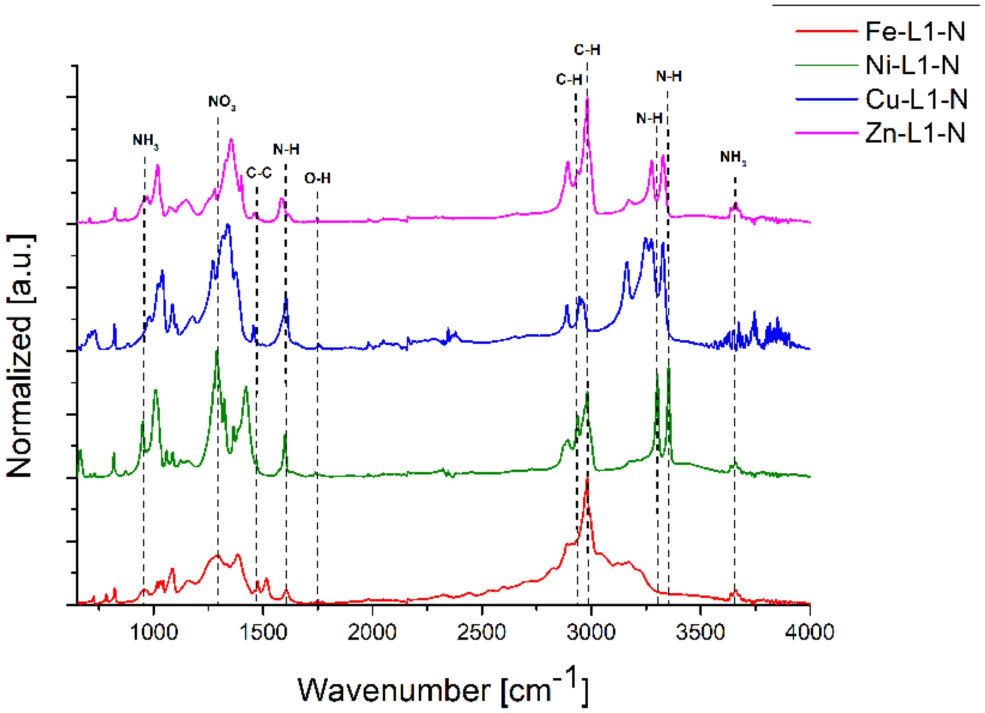

Figure 59: IR-ATR spectra for energetic coordination compounds containing 1,2-ethylenediamine and nitrate salts.

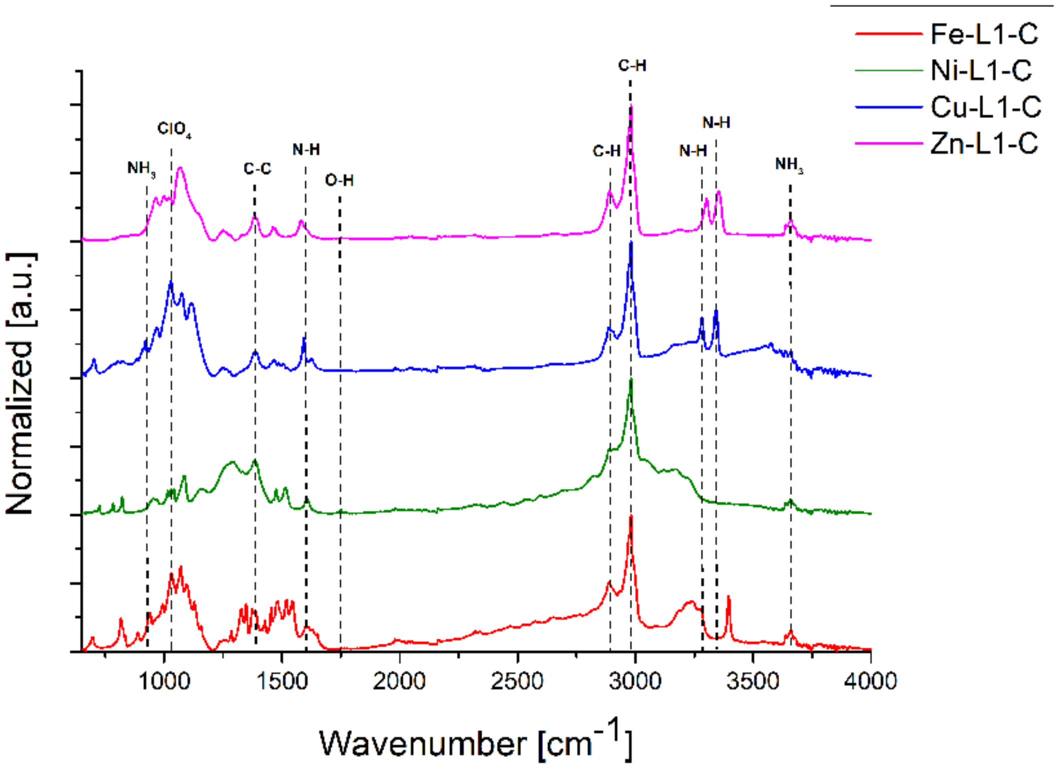

Figure 60: IR-ATR spectra for energetic coordination compounds containing 1,2-ethylenediamine and perchlorate salts.

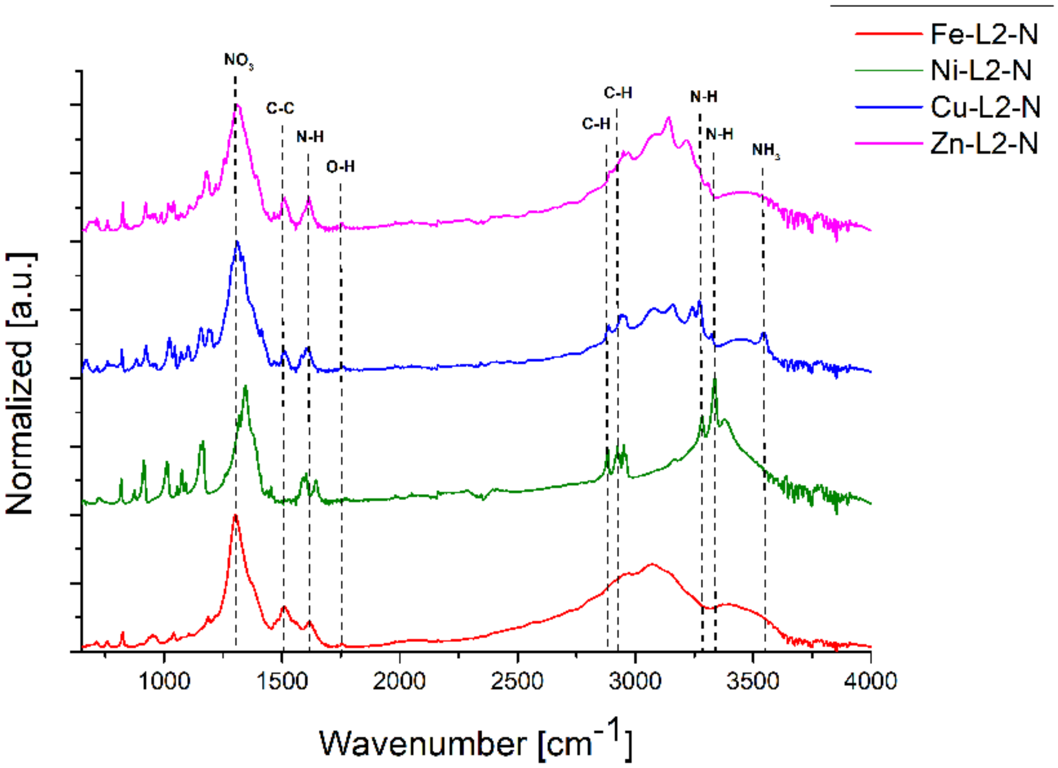

Figure 61: IR-ATR spectra for energetic coordination compounds containing 1,3-diaminopropane and nitrate salts.

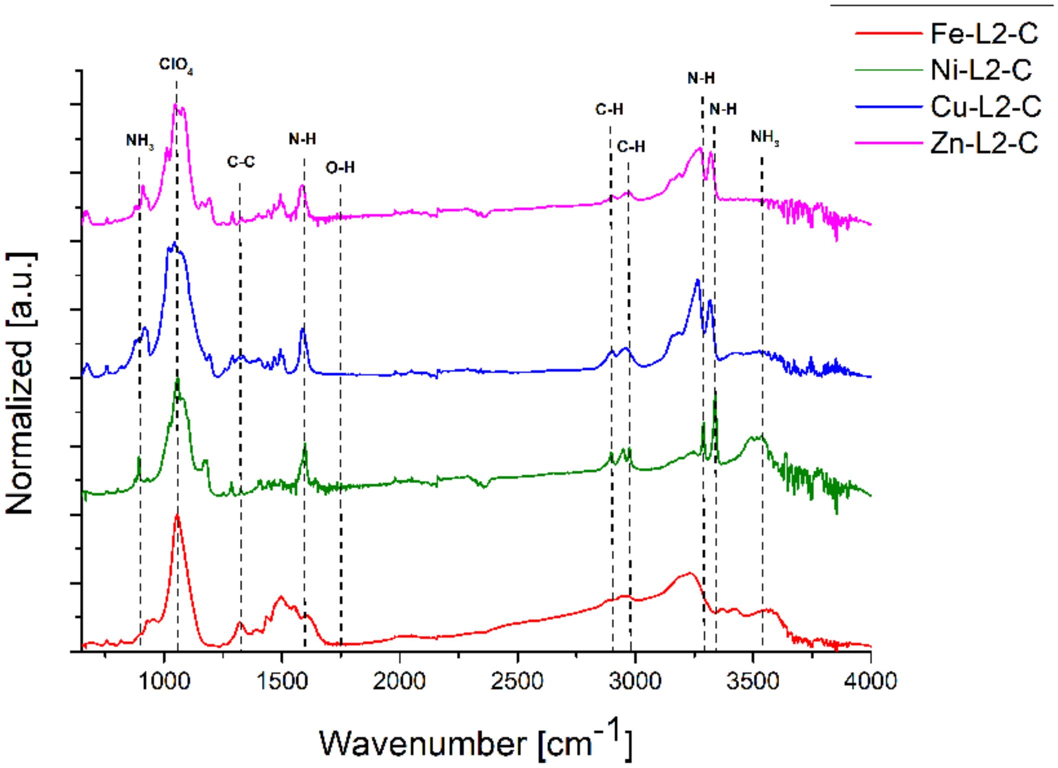

Figure 62: IR-ATR spectra for energetic coordination compounds containing 1,3-diaminopropane and perchlorate salts.

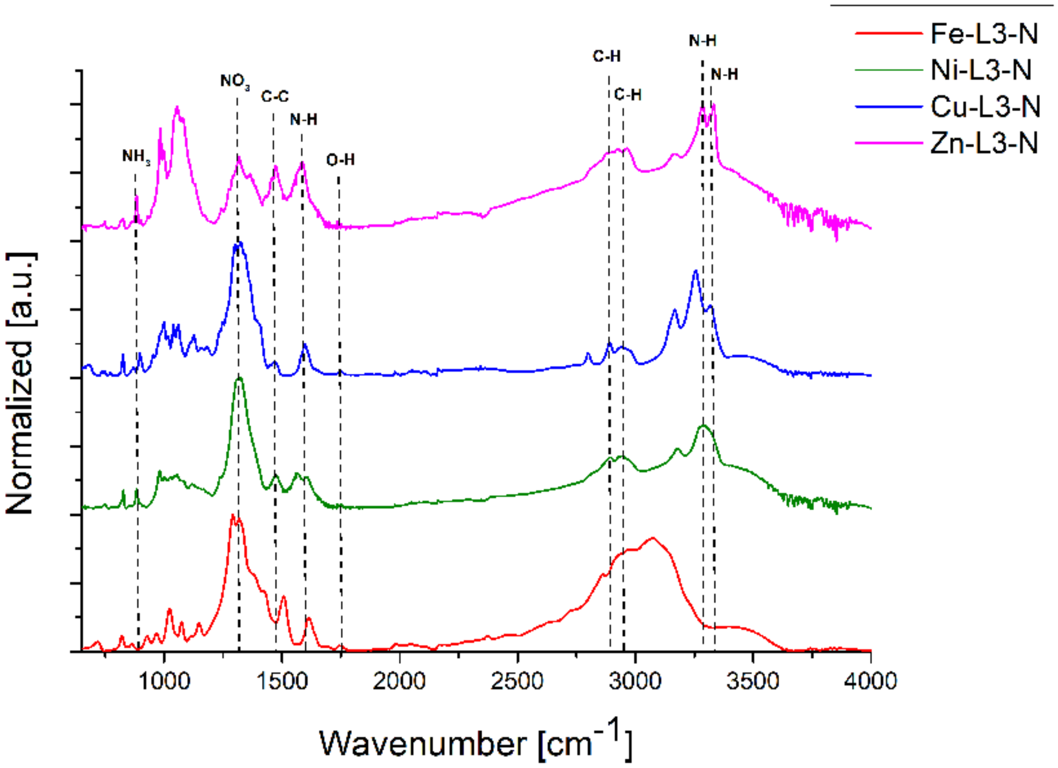

Figure 63: IR-ATR spectra for energetic coordination compounds containing tris(2-aminoethyl)amine and nitrate salts.

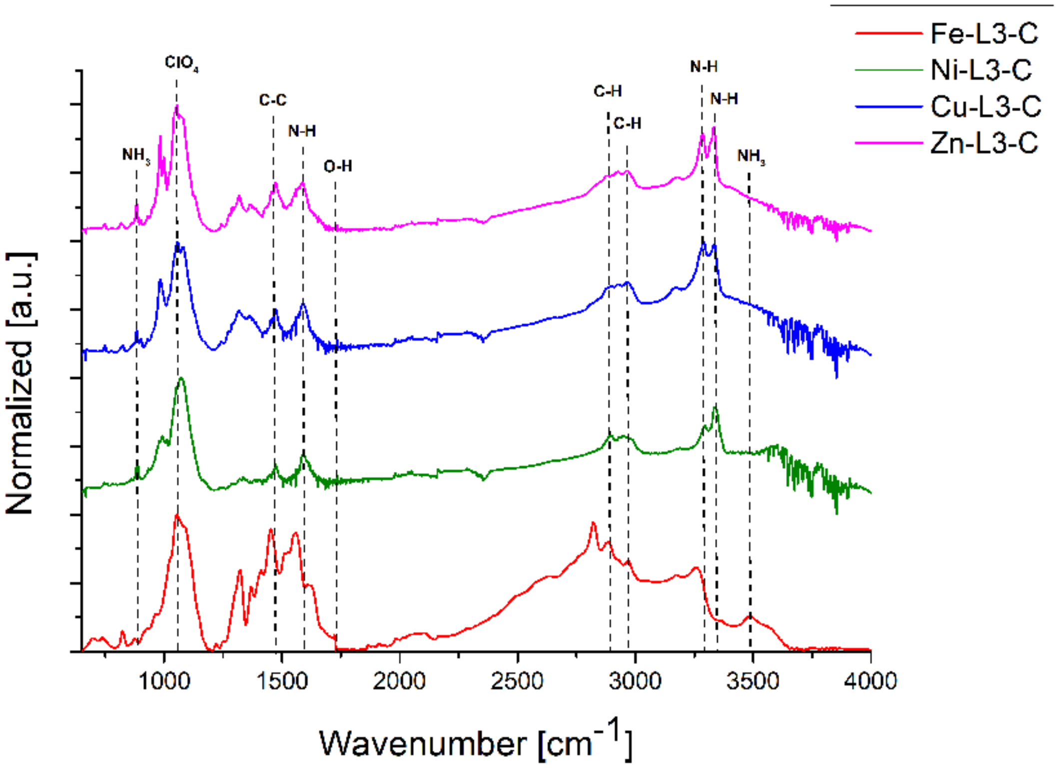

Figure 64: IR-ATR spectra for energetic coordination compounds containing tris(2-aminoethyl)amine and perchlorate salts.

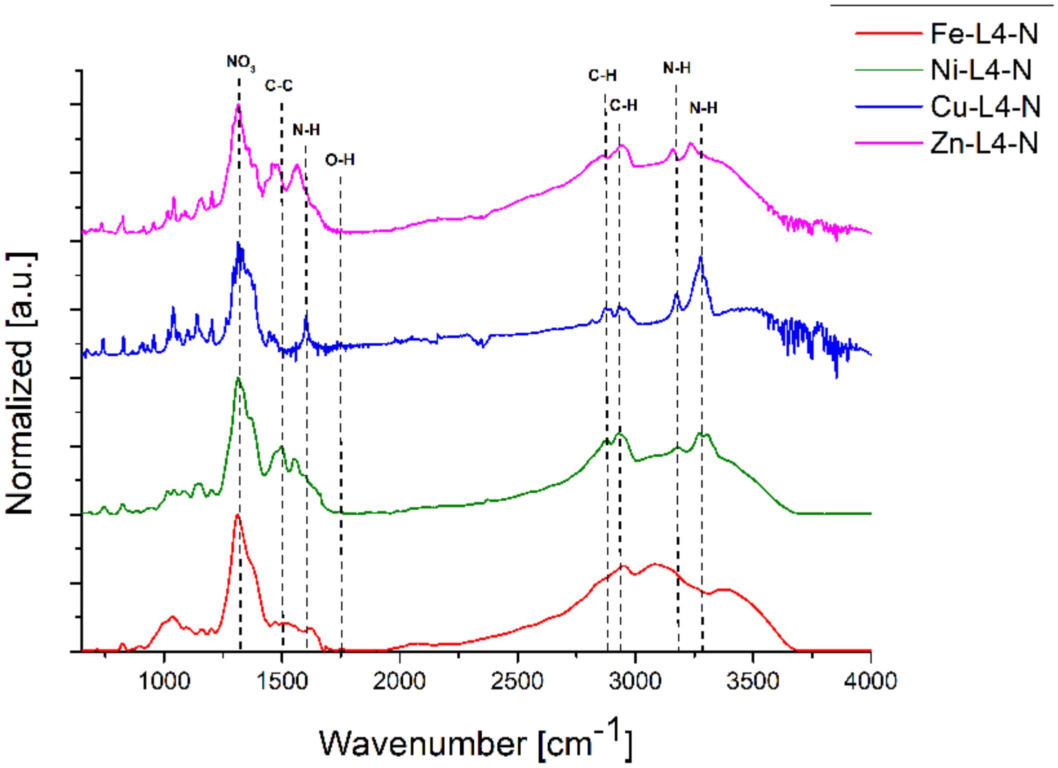

Figure 65: IR-ATR spectra for energetic coordination compounds containing tris(3-aminopropyl)amine and nitrate salts.

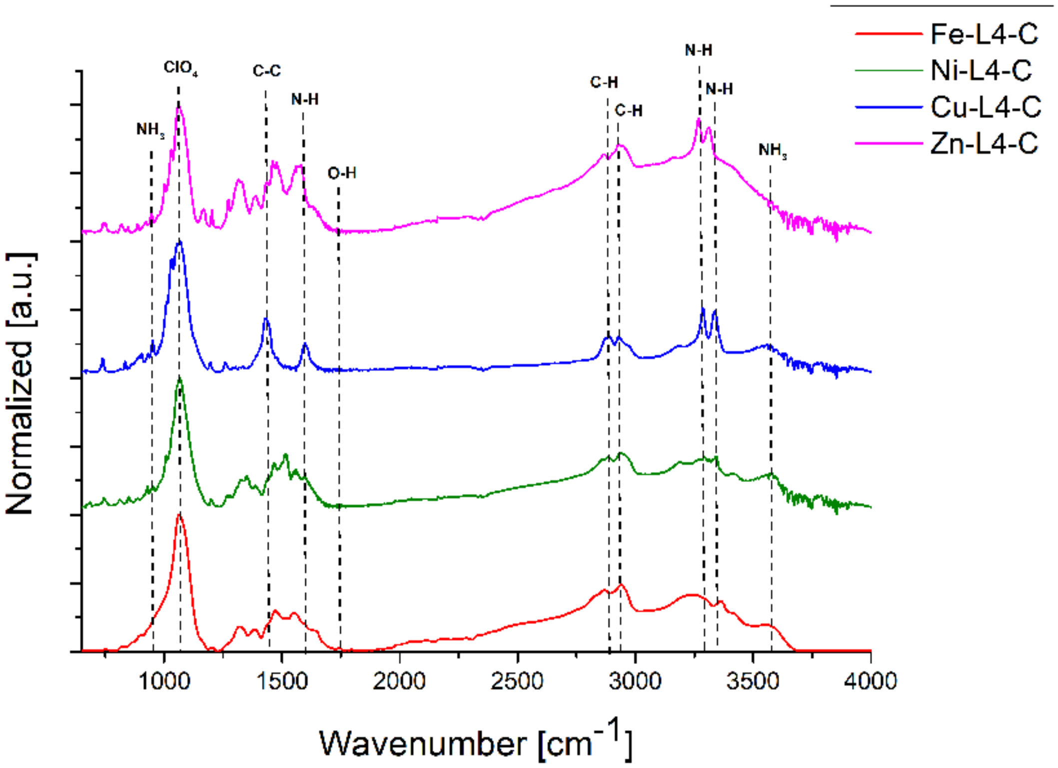

Figure 66: IR-ATR spectra for energetic coordination compounds containing tris(3-aminopropyl)amine and perchlorate salts.

The tables (Tab. 36, 37, 38, 39) show the values of characteristic absorption bands derived from the groups and bonds present in the obtained compounds.

Table 36: Results from IR-ATR measurements for ECCs containing 1,2-ethylenediamine.

Sample code	**Wavenumber [cm^{-1}]**					
	NO_3^-/ClO_4^-	**C−C**	**N−H**	**O−H**	**C−H**	**NH_3**
Fe-L1-N	1296	1475	1608, 3221	1749	2971, 2981	958, 3660
Ni-L1-N	1290	1471	1601, 3301, 3354	1741	2981, 2983	952, 3660
Cu-L1-N	1340	1458	1604, 3274, 3328	1753	2888, 2946	982, 3672
Zn-L1-N	1352	1464	1586, 3274, 3328	1749	2892, 2982	971, 3661
Fe-L1-C	1073	1375	1603, 3245, 3396	-	2890, 2981	942, 3658
Ni-L1-C	1086	1383	1607, 3221	1750	2889, 2982	954, 3661
Cu-L1-C	1030	1391	1594, 3282, 3342	-	2892, 2982	972, 3661
Zn-L1-C	1068	1385	1581, 3303, 3353	-	2894, 2981	969, 3661

Table 37: Results from IR-ATR measurements for ECCs containing 1,3-diaminopropane.

Sample code	**Wavenumber [cm^{-1}]**					
	NO_3^-/ClO_4^-	**C−C**	**N−H**	**O−H**	**C−H**	**NH_3**
Fe-L2-N	1303	1510	1620, -	1752	-	-
Ni-L2-N	1347	1454	1602, 3283, 3336	1772	2882, 2925	-
Cu-L2-N	1314	1512	1603, 3273, 3326	1761	2886, 2945	3547
Zn-L2-N	1312	1511	1616, 3220, 3311	1756	2891, 2949	-
Fe-L2-C	1056	1325	1609, 3273	-	2883, 2947	927, 3561
Ni-L2-C	1057	1327	1599, 3289, 3339	1734	2899, 2975	892, 3537
Cu-L2-C	1047	1320	1585, 3265, 3316	-	2900, 2963	920, 3526
Zn-L2-C	1047	1293	1588, 3276, 3320	-	2903, 2977	910, -

Table 38: Results from IR-ATR measurements for ECCs containing tris(2-aminoethyl)amine.

Sample code	**Wavenumber [cm^{-1}]**					
	NO_3^-/ClO_4^-	**C−C**	**N−H**	**O−H**	**C−H**	**NH_3**
Fe-L3-N	1296	1512	1618, -	1744	2860, 2968	928
Ni-L3-N	1328	1475	1601, 3281	1751	2889, 2943	884
Cu-L3-N	1326	1477	1595, 3260, 3322	1750	2895, 2940	900
Zn-L3-N	1322	1476	1586, 3282, 3329	1752	2919, 2966	885
Fe-L3-C	1056	1454	1564, 3262	1722	2878, 2970	876, 3488
Ni-L3-C	1072	1475	1588, 3292, 3337	1752	2897, 2953	887
Cu-L3-C	1053	1475	1592, 3288, 3337	1751	2900, 2962	884
Zn-L3-C	1056	1473	1585, 3286, 3333	1734	2877, 2961	883

Table 39: Results from IR-ATR measurements for ECCs containing tris(3-aminopropyl)amine.

Sample code	**Wavenumber [cm^{-1}]**					
	NO_3^-/ClO_4^-	**C−C**	**N−H**	**O−H**	**C−H**	**NH_3**
Fe-L4-N	1314	1480	1624, 3374	1750	2950	-
Ni-L4-N	1310	1498	1558, 3182, 3272	1748	2878, 2930	-
Cu-L4-N	1315	1449	1603, 3178, 3277	-	2872, 2930	-
Zn-L4-N	1317	1468	1569, 3157, 3238	-	2858, 2944	-
Fe-L4-C	1068	1472	1648, 3244, 3365	1744	2870, 2940	-, 3568
Ni-L4-C	1070	1465	1559, 3286, 3343	-	2888, 2933	931, 3576
Cu-L4-C	1069	1428	1600, 3288, 3341	-	2876, 2930	952, 3558

Raman spectroscopy

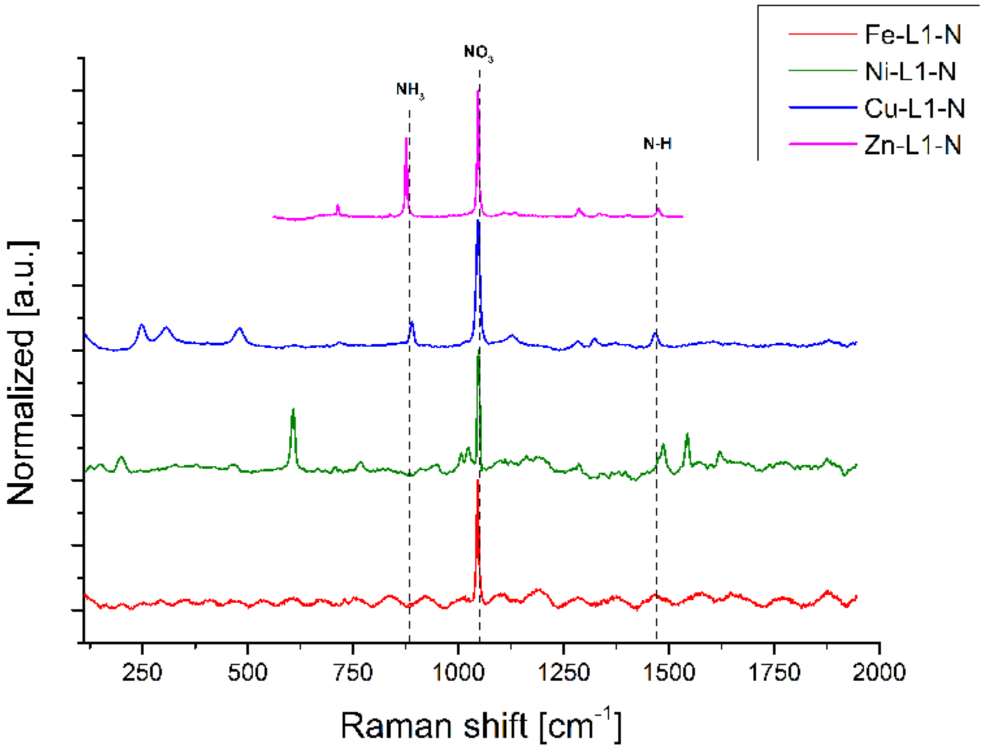

Figure 67: Raman spectra for energetic coordination compounds containing 1,2-ethylenediamine and nitrate anion.

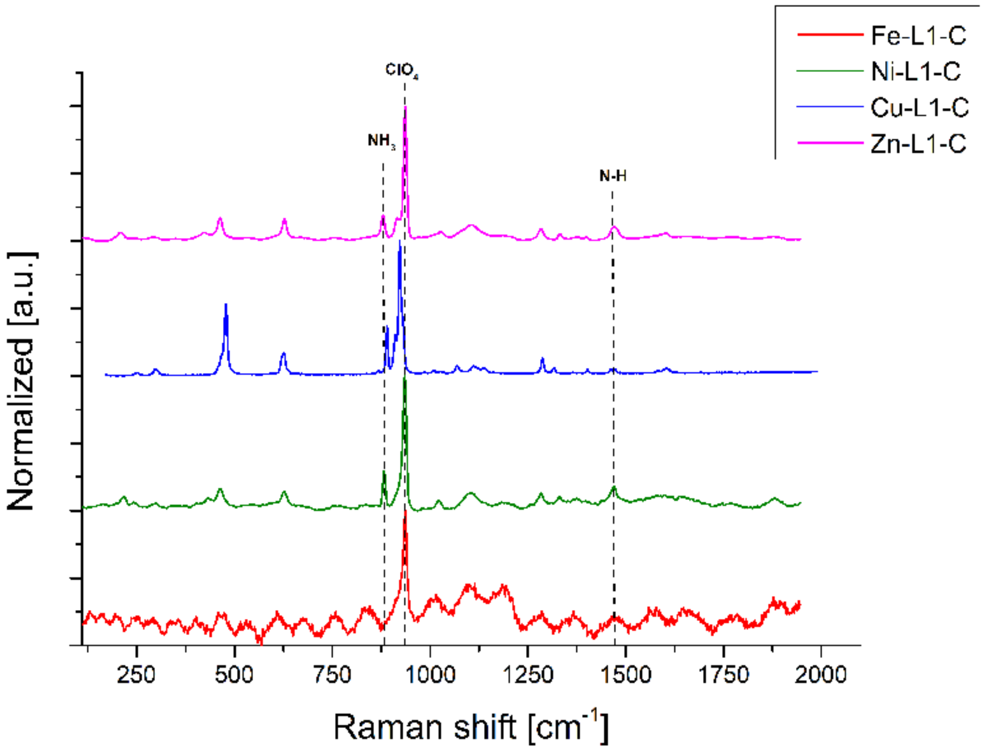

Figure 68: Raman spectra for energetic coordination compounds containing 1,2-ethylenediamine and perchlorate anion.

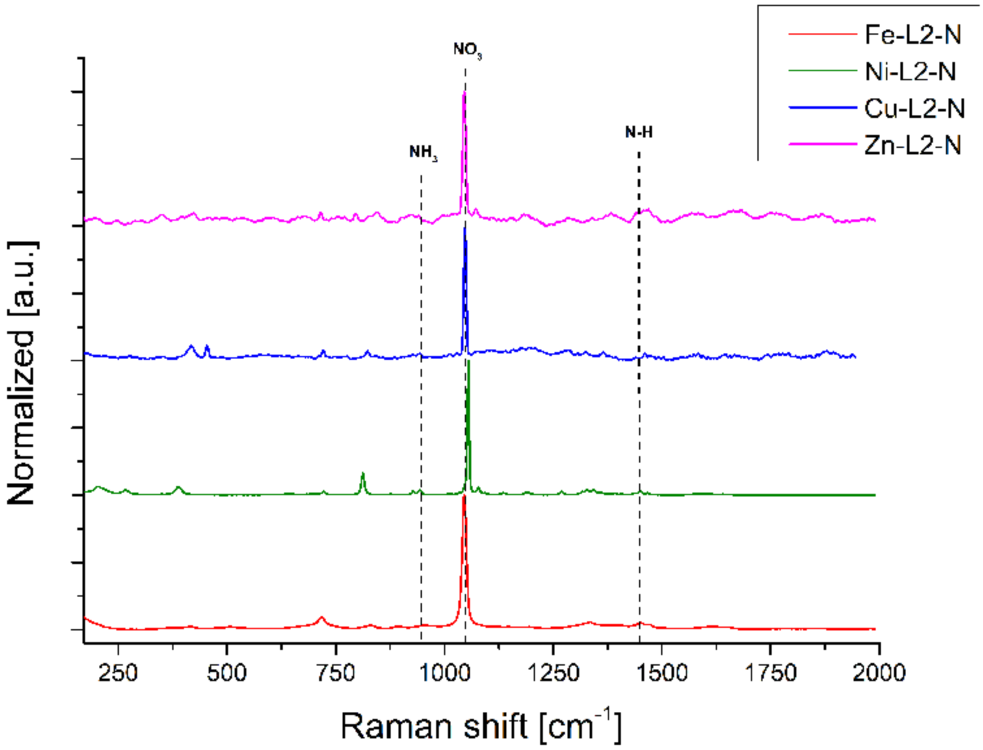

Figure 69: Raman spectra for energetic coordination compounds containing 1,3-diaminopropane and nitrate anion.

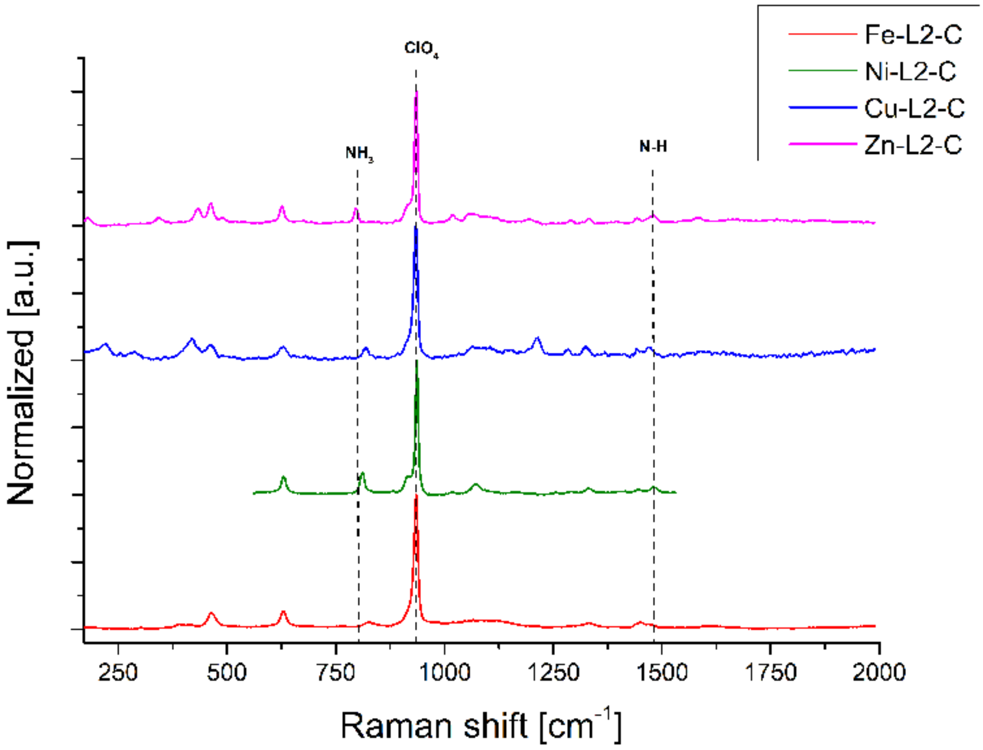

Figure 70: Raman spectra for energetic coordination compounds containing 1,3-diaminopropane and perchlorate anion.

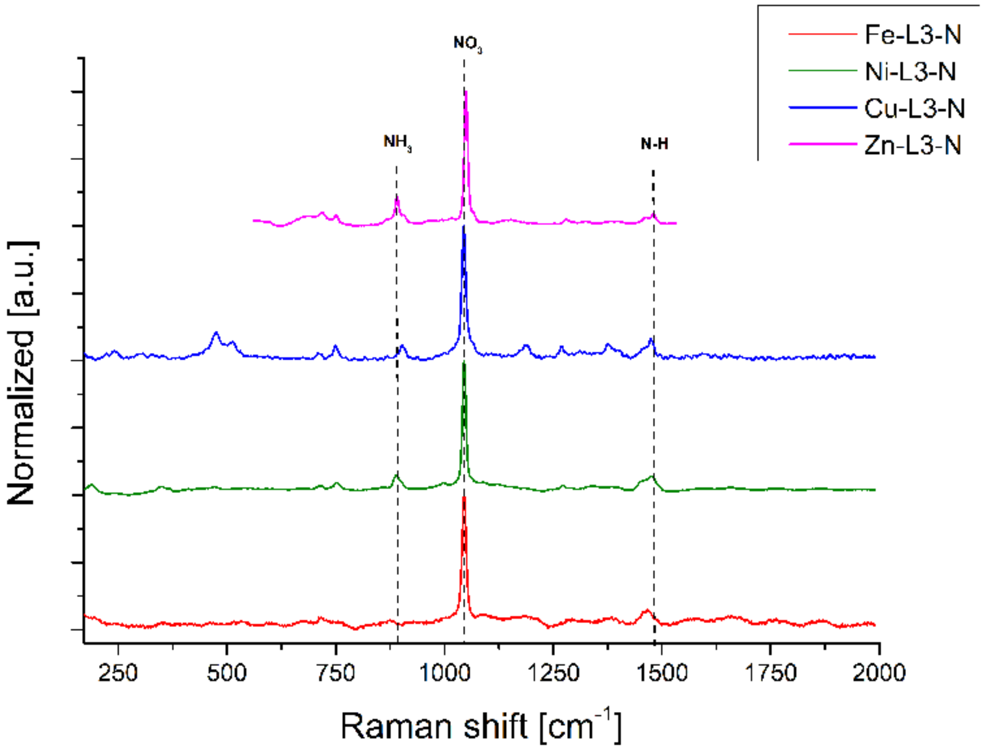

Figure 71: Raman spectra for energetic coordination compounds containing tris(2-aminoethyl)amine and nitrate anion.

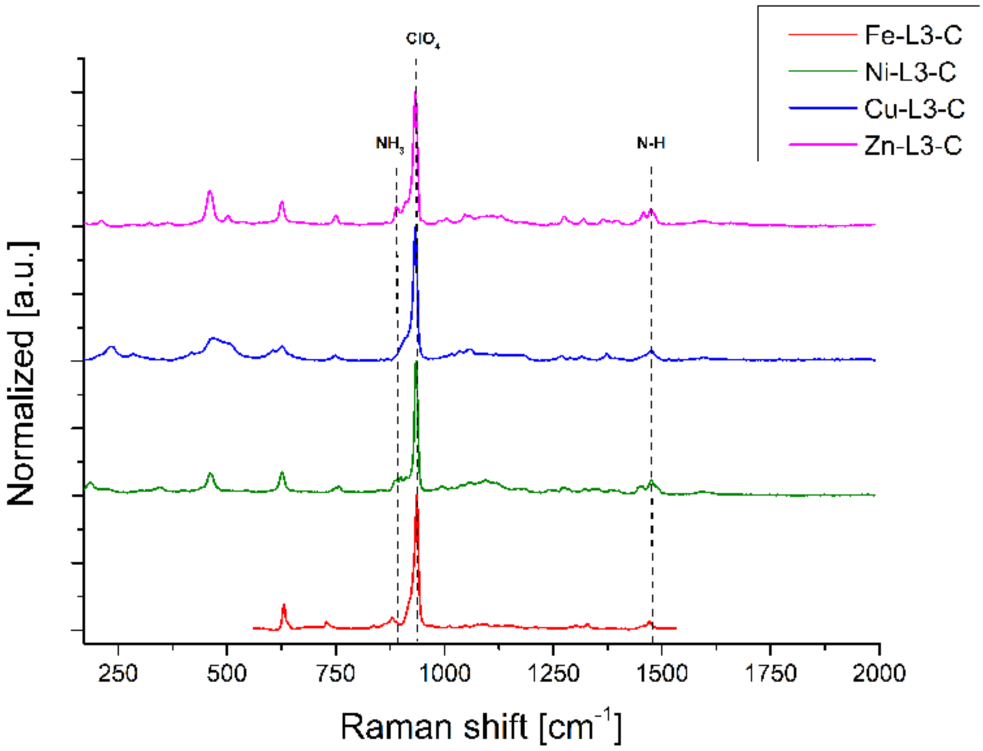

Figure 72: Raman spectra for energetic coordination compounds containing tris(2-aminoethyl)amine and perchlorate anion.

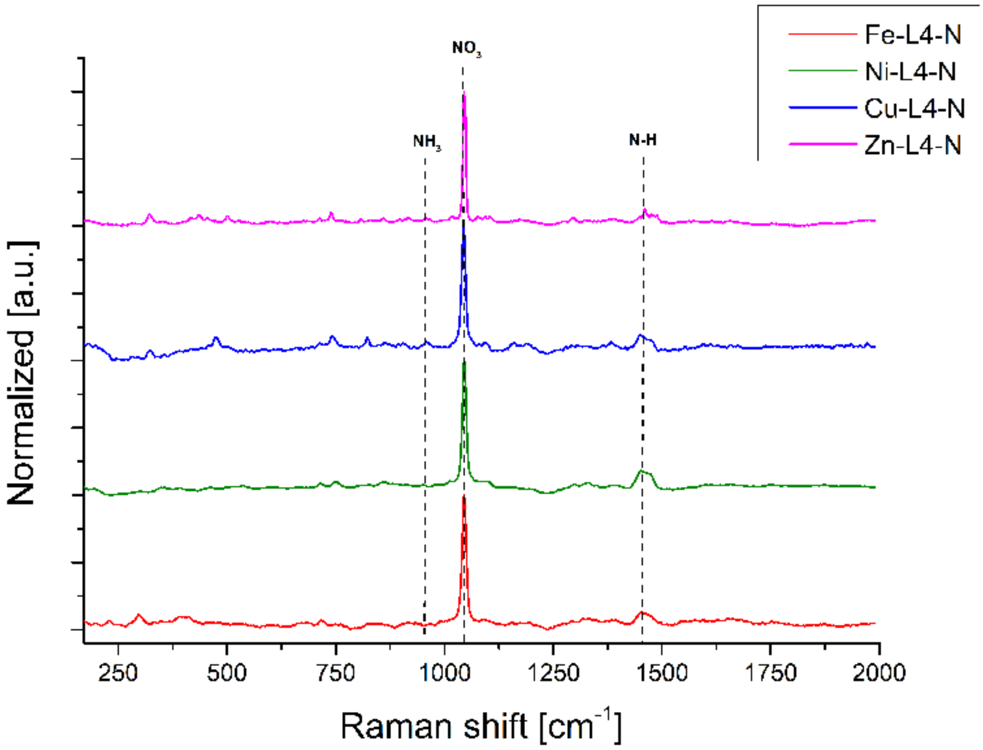

Figure 73: Raman spectra for energetic coordination compounds containing tris(3-aminopropyl)amine and nitrate anion.

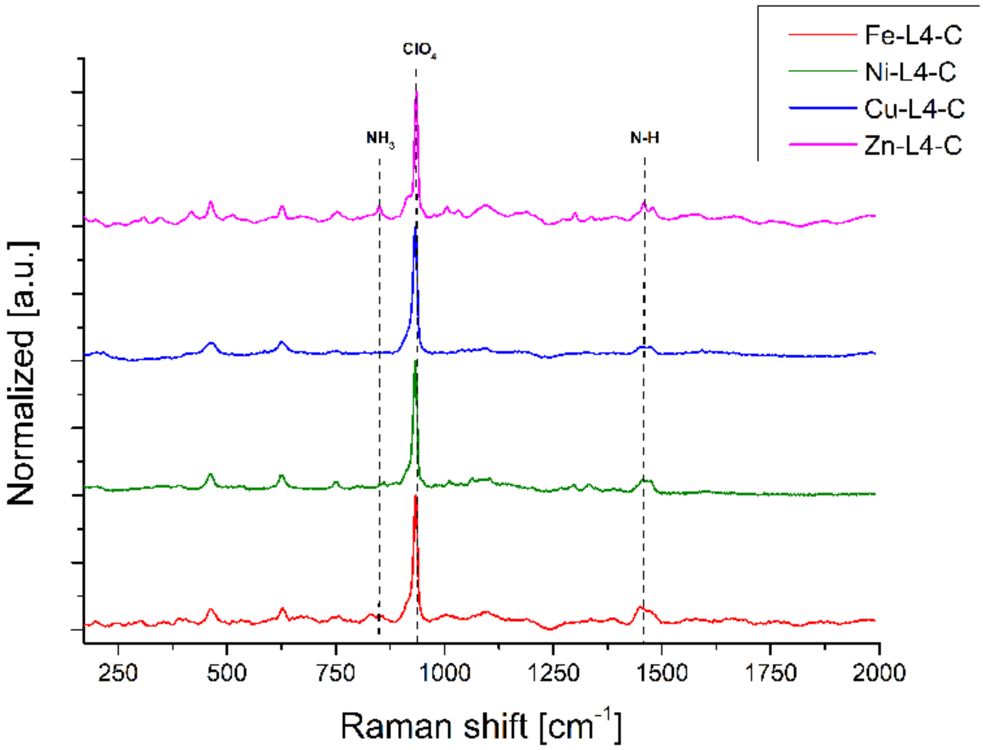

Figure 74: Raman spectra for energetic coordination compounds containing tris(3-aminopropyl)amine and perchlorate anion.

Scanning electron microscopy

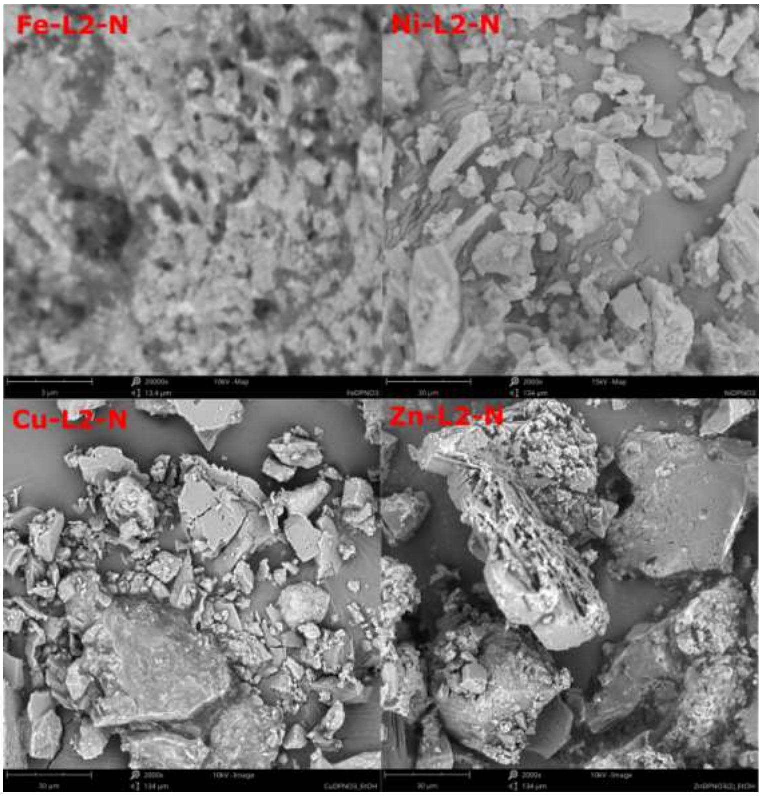

Figure 75: SEM images of ECCs containing 1,3-diaminopropane and nitrate anion.

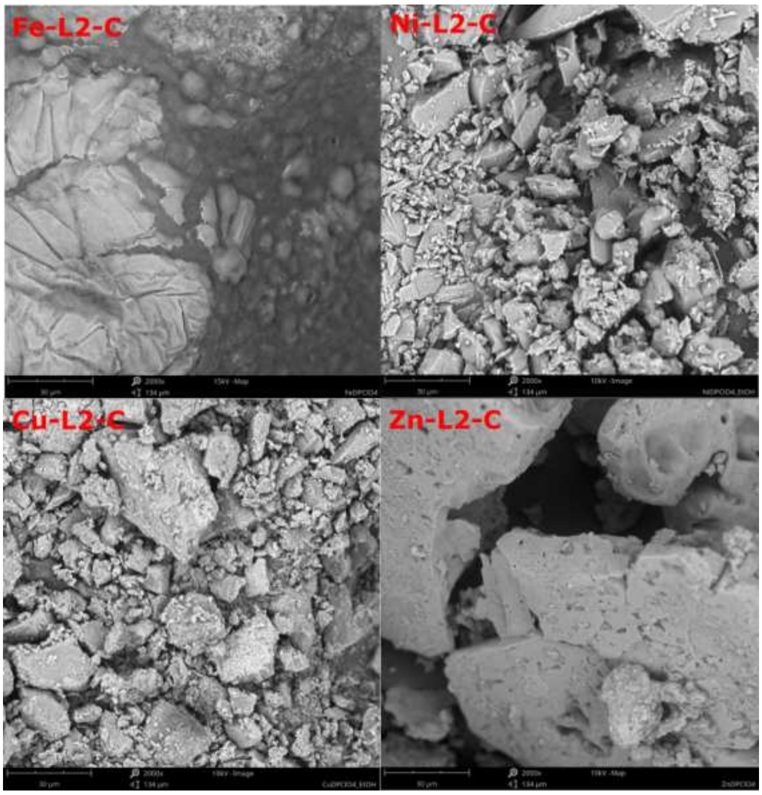

Figure 76: SEM images of ECCs containing 1,3-diaminopropane and perchlorate anion.

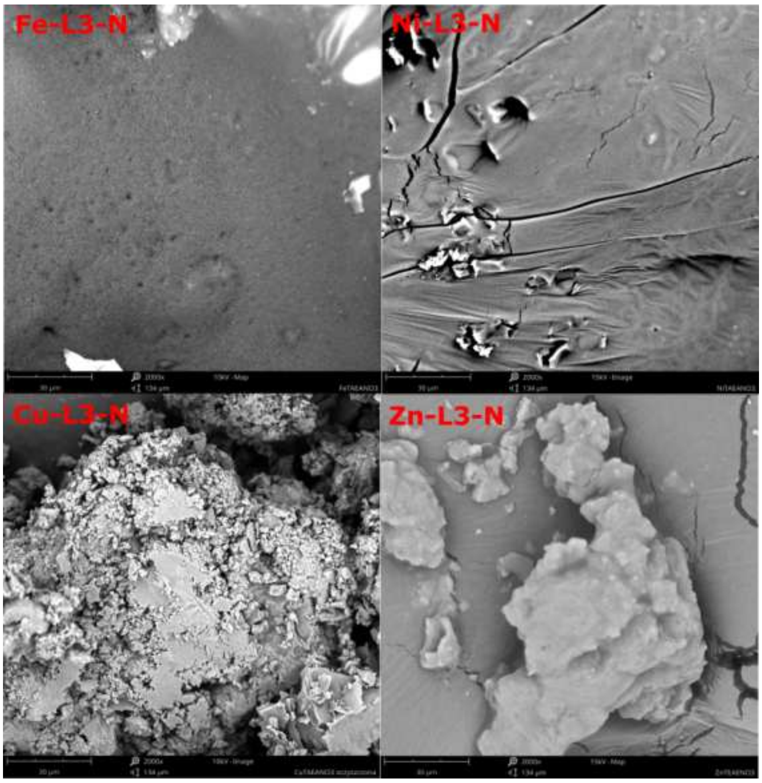

Figure 77: SEM images of ECCs containing tris(2-aminoethyl)amine and nitrate anion.

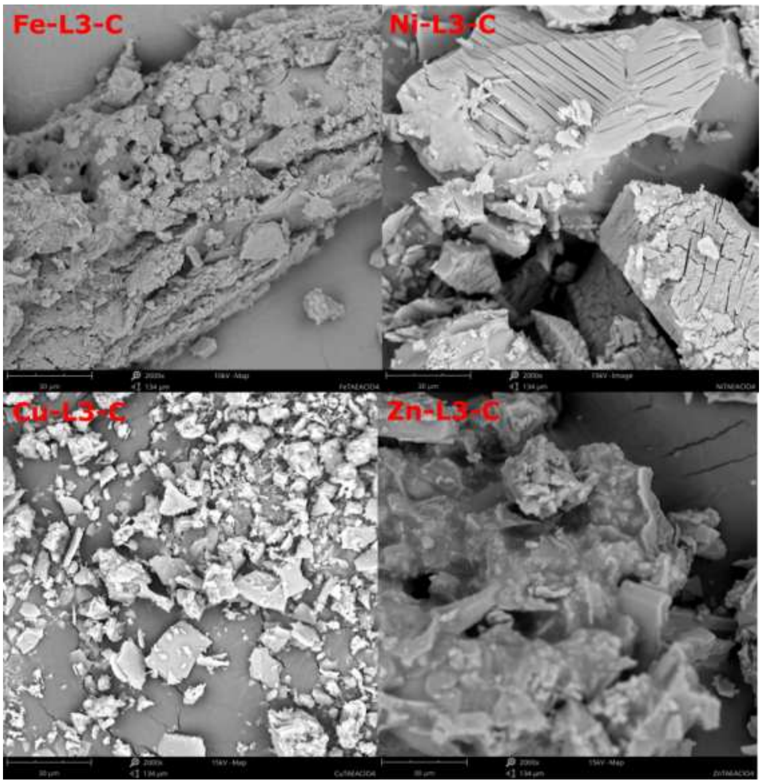

Figure 78: SEM images of ECCs containing tris(2-aminoethyl)amine and perchlorate anion.

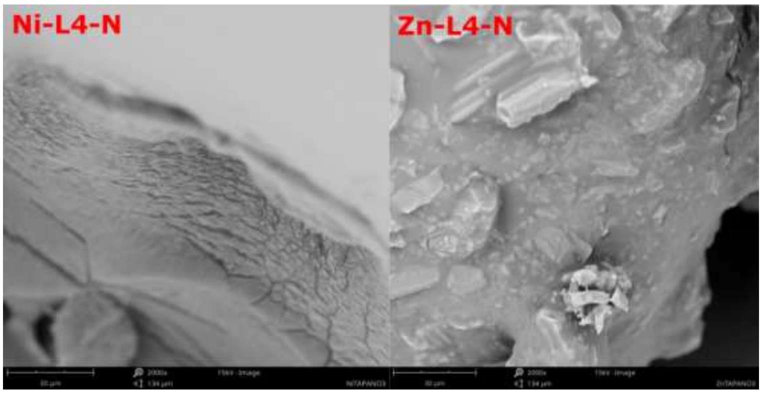

Figure 79: SEM images of ECCs containing tris(3-aminopropyl)amine and nitrate anion.

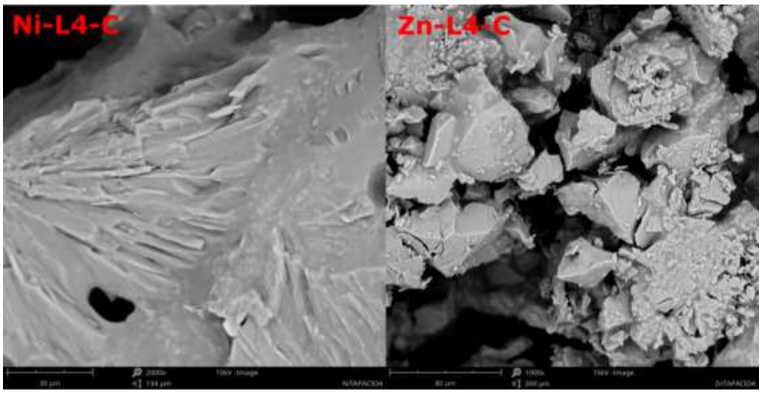

Figure 80: SEM images of ECCs containing tris(3-aminopropyl)amine and perchlorate anion.

Powder X-ray diffractometry

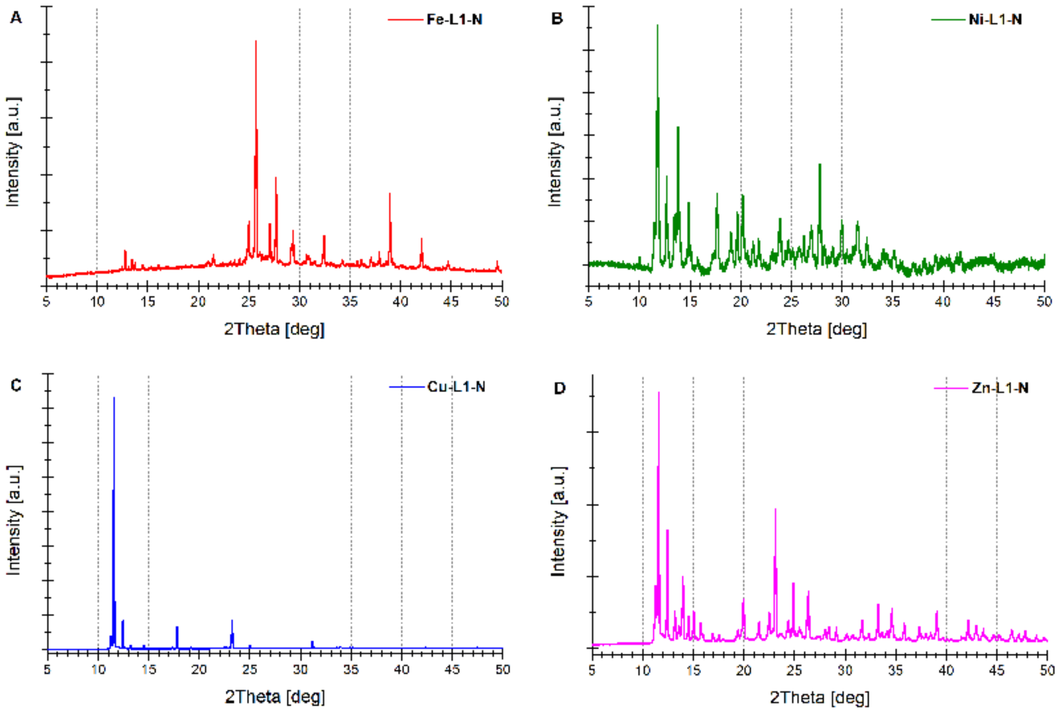

Figure 81: Powder X-ray diffraction patterns for ECCs containing 1,2-ethylenediamine and nitrate analogues.

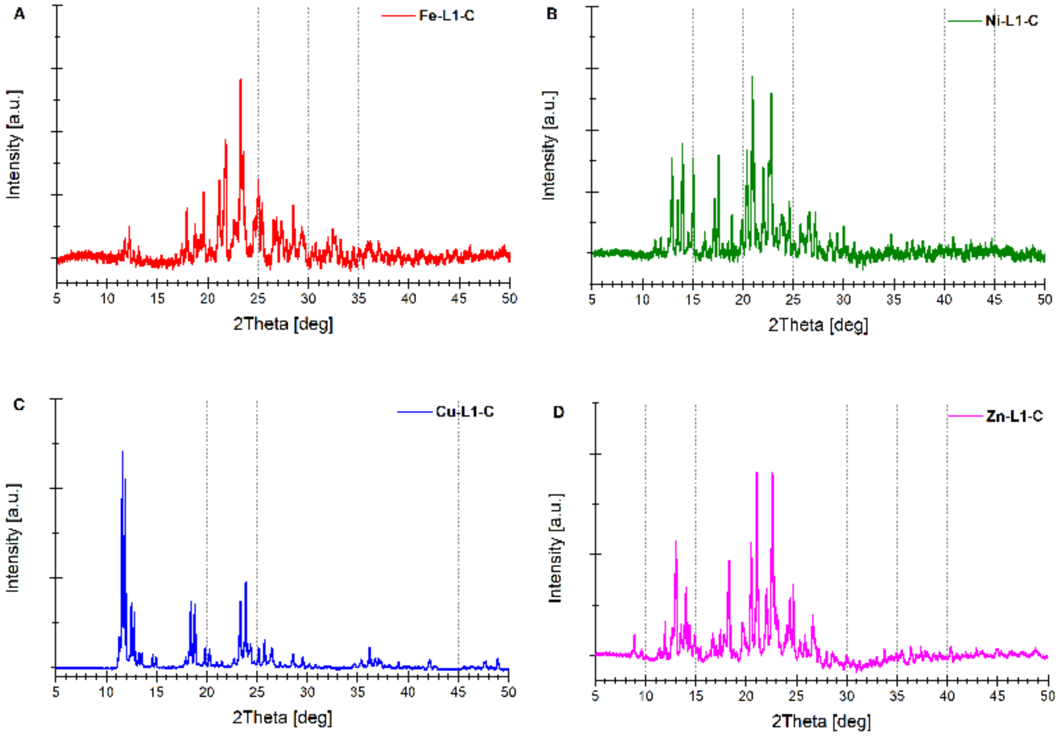

Figure 82: Powder X-ray diffraction patterns for ECCs containing 1,2-ethylenediamine and perchlorate analogues.

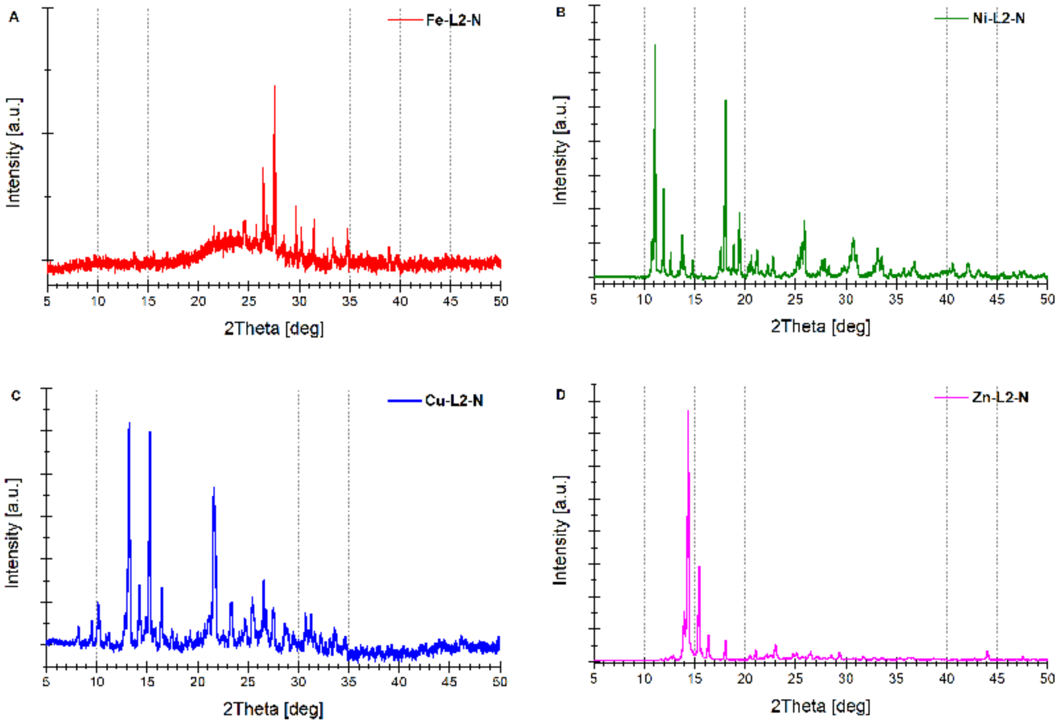

Figure 83: Powder X-ray diffraction patterns for ECCs containing 1,3-diaminopropane and nitrate analogues.

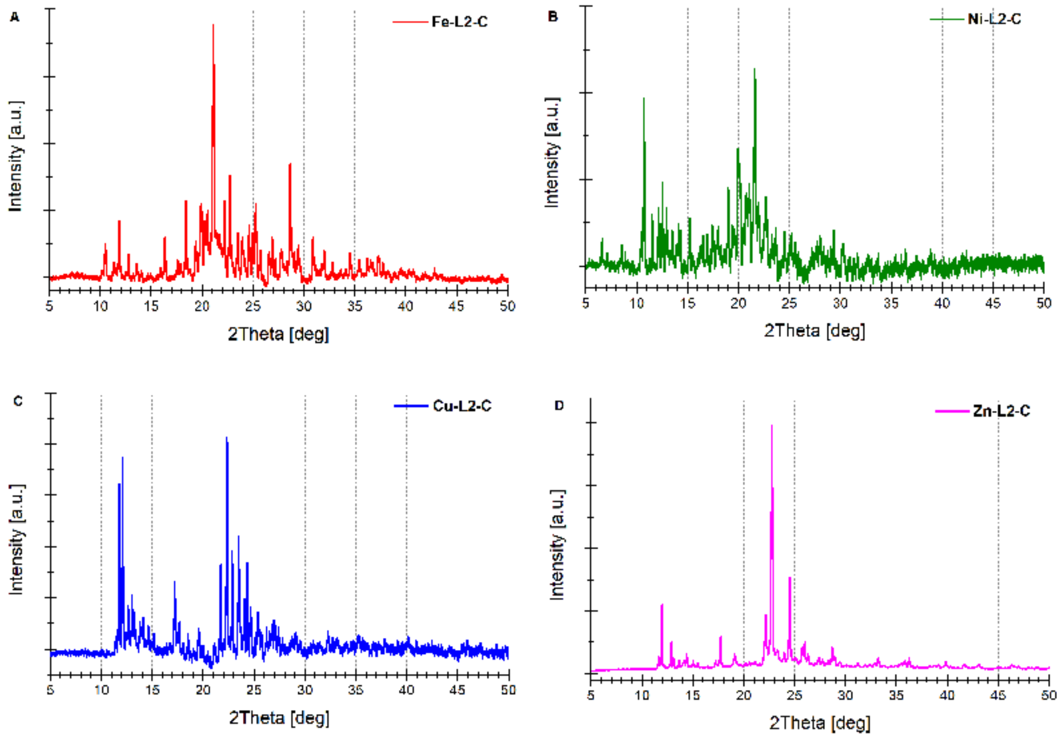

Figure 84: Powder X-ray diffraction patterns for ECCs containing 1,3-diaminopropane and perchlorate analogues.

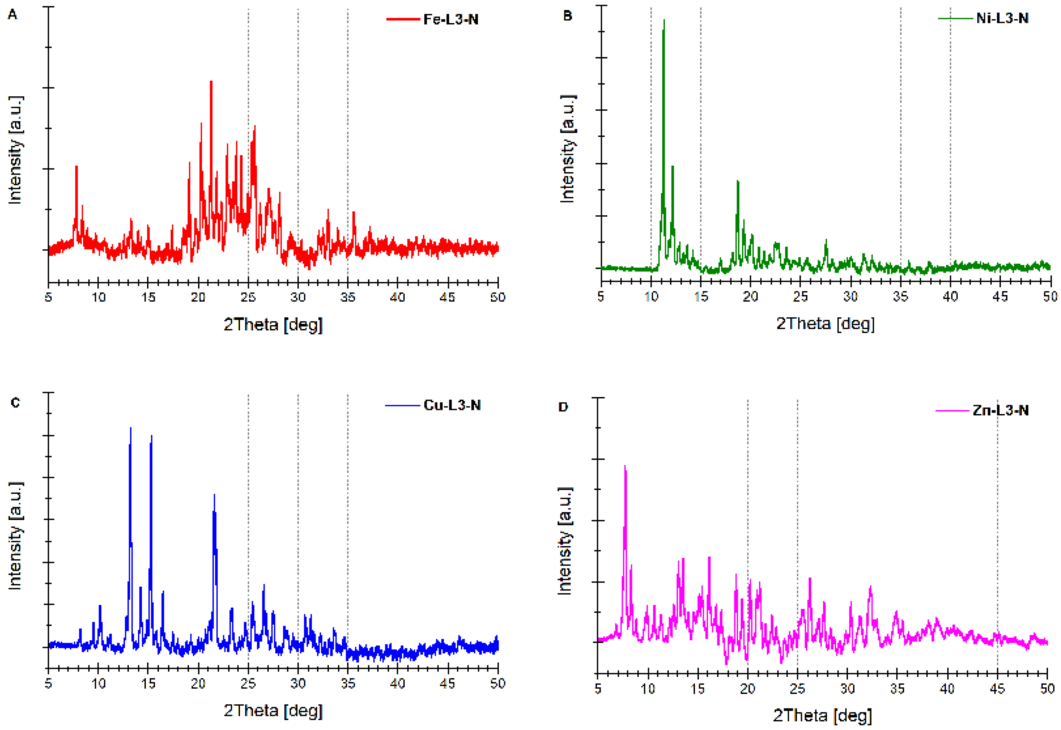

Figure 85: Powder X-ray diffraction patterns for ECCs containing tris(2-aminoethyl)amine and nitrate analogues.

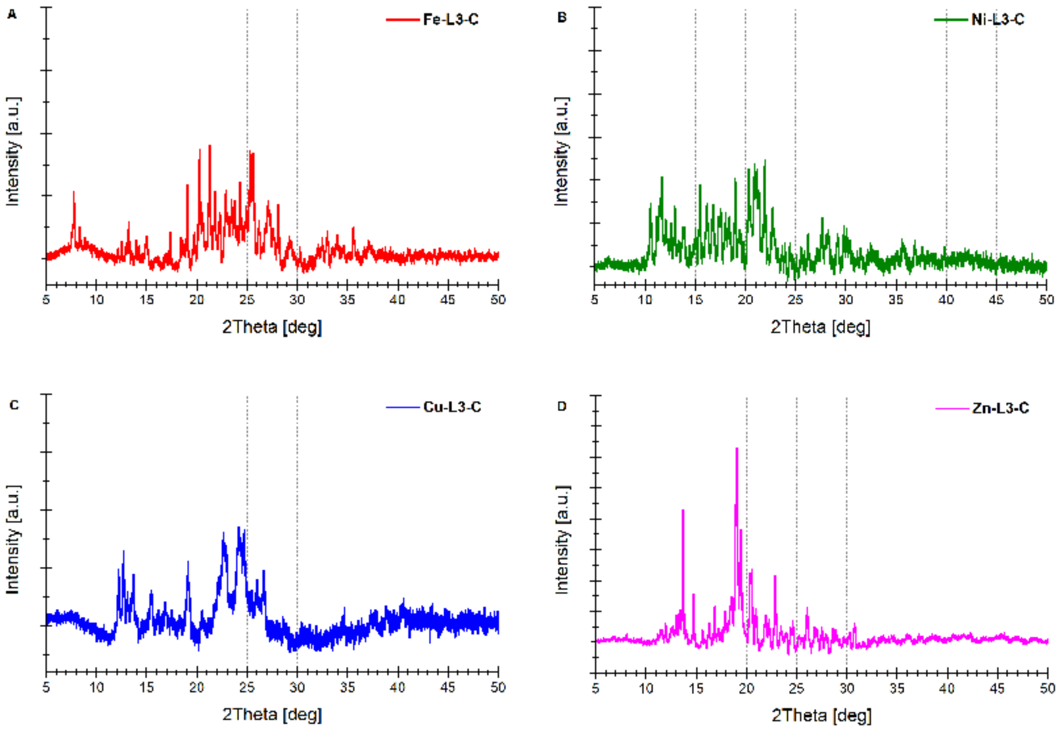

Figure 86: Powder X-ray diffraction patterns for ECCs containing tris(2-aminoethyl)amine and perchlorate analogues.

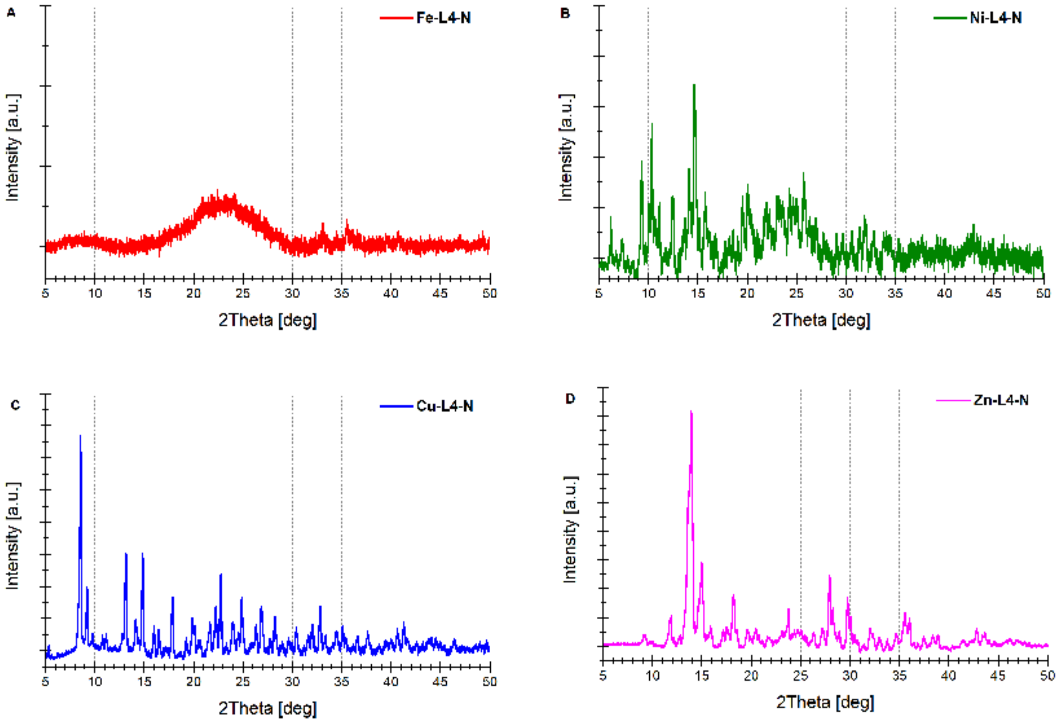

Figure 87: Powder X-ray diffraction patterns for ECCs containing tris(3-aminopropyl)amine and nitrate analogues.

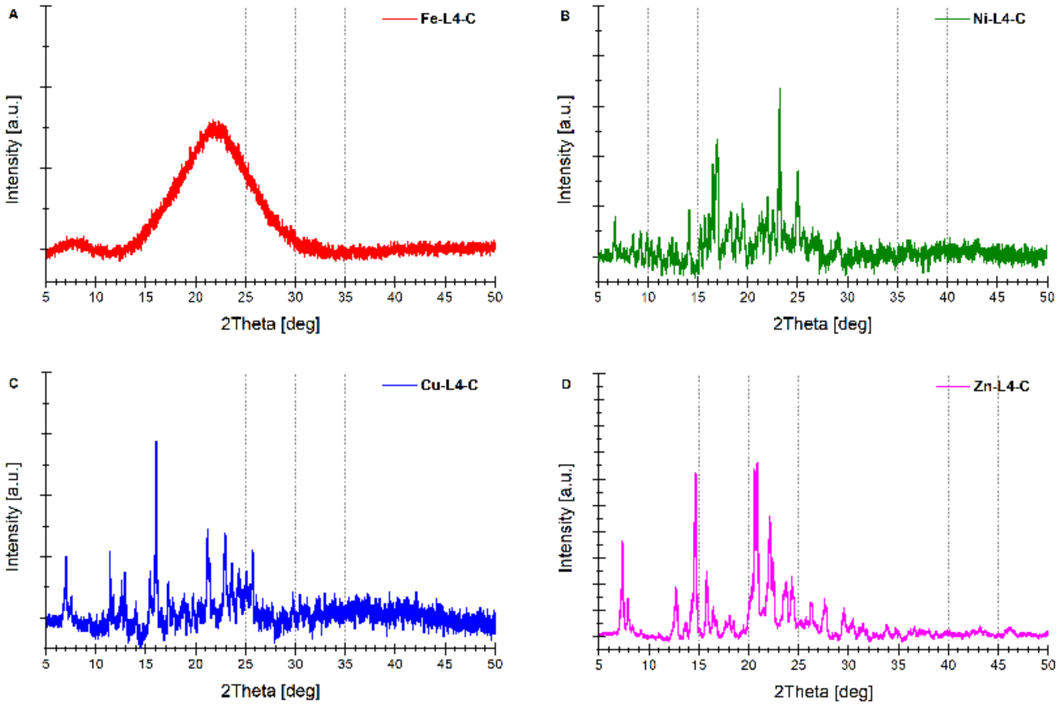

Figure 88: Powder X-ray diffraction patterns for ECCs containing tris(3-aminopropyl)amine and perchlorate analogues.

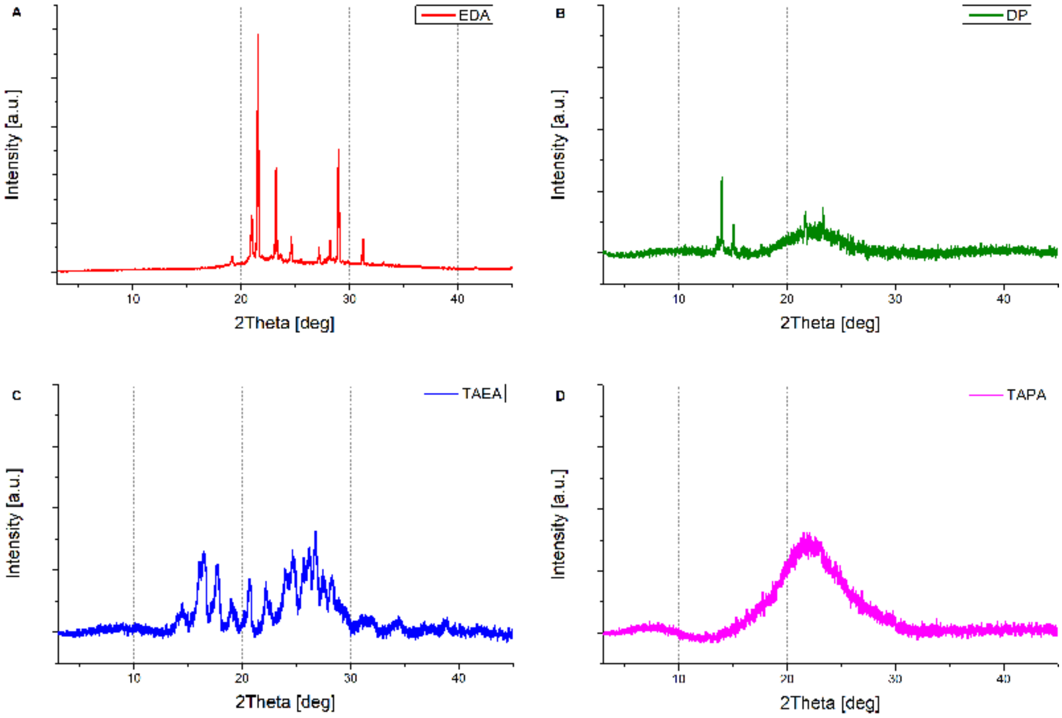

Figure 89: Powder X-ray diffraction patterns for ligands used for synthesis of ECCs.

Cyclic voltammetry

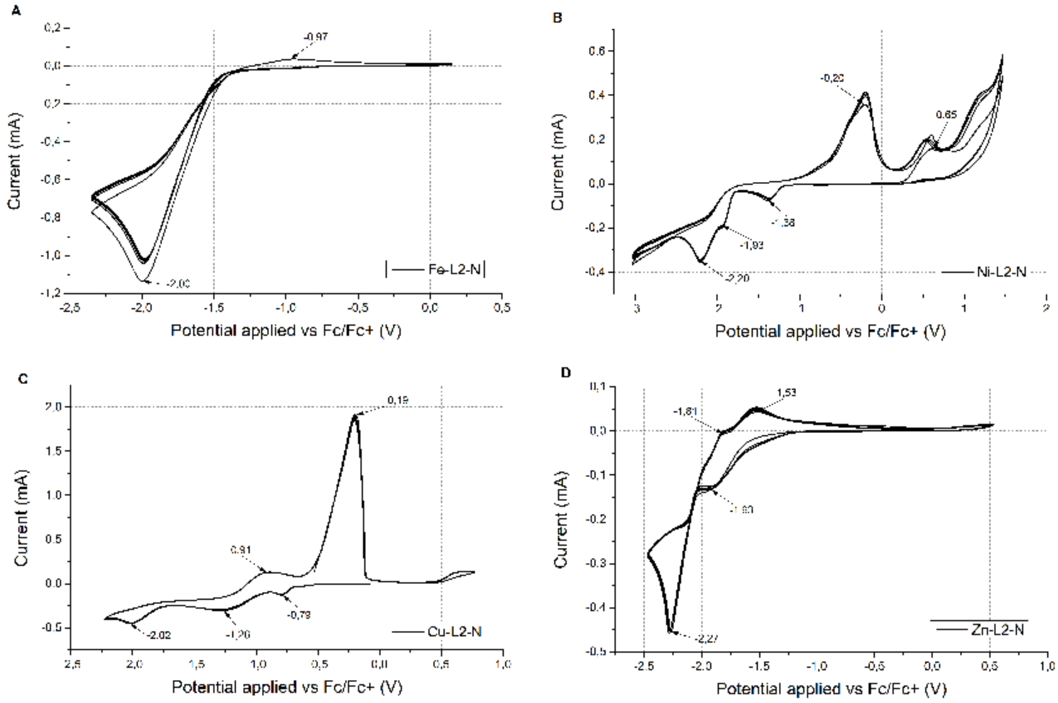

Figure 90: Voltammogram for ECCs containing 1,3-diaminopropane and corresponding nitrate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

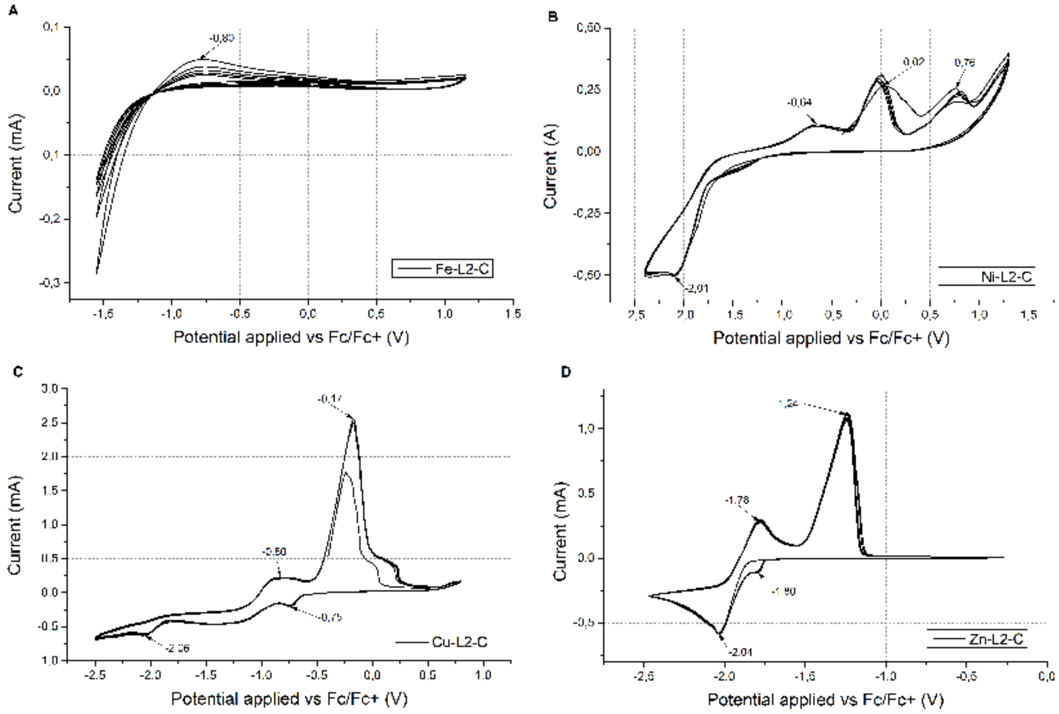

Figure 91: Voltammogram for ECCs containing 1,3-diaminopropane and corresponding perchlorate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

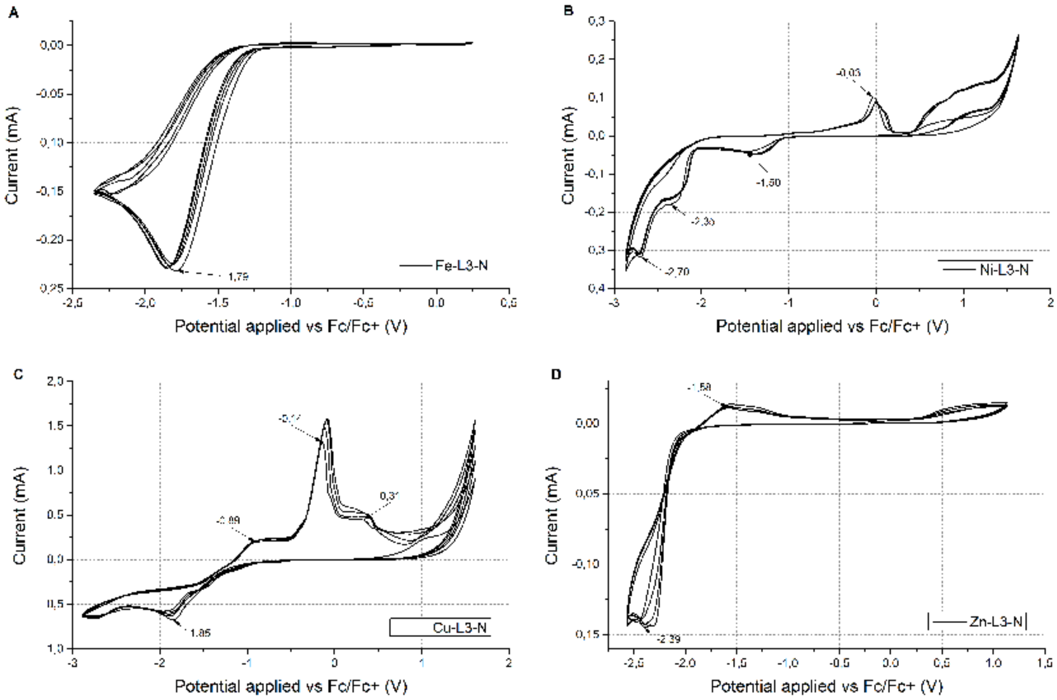

Figure 92: Voltammogram for ECCs containing tris(2-aminoethyl)amine and corresponding nitrate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

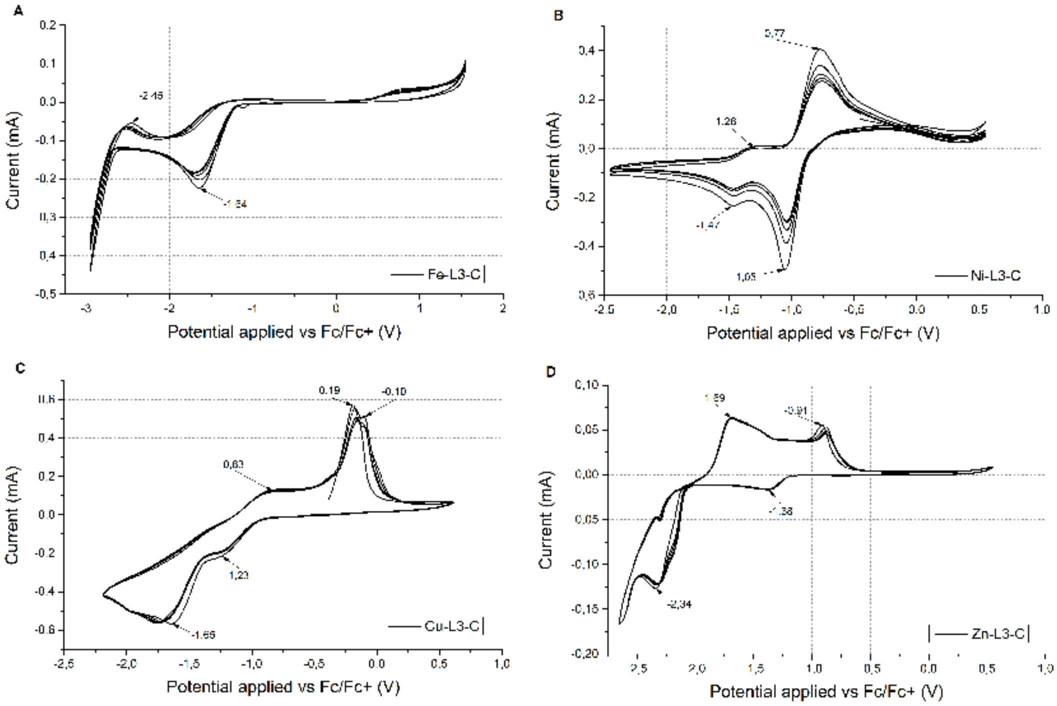

Figure 93: Voltammogram for ECCs containing tris(2-aminoethyl)amine and corresponding nitrate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

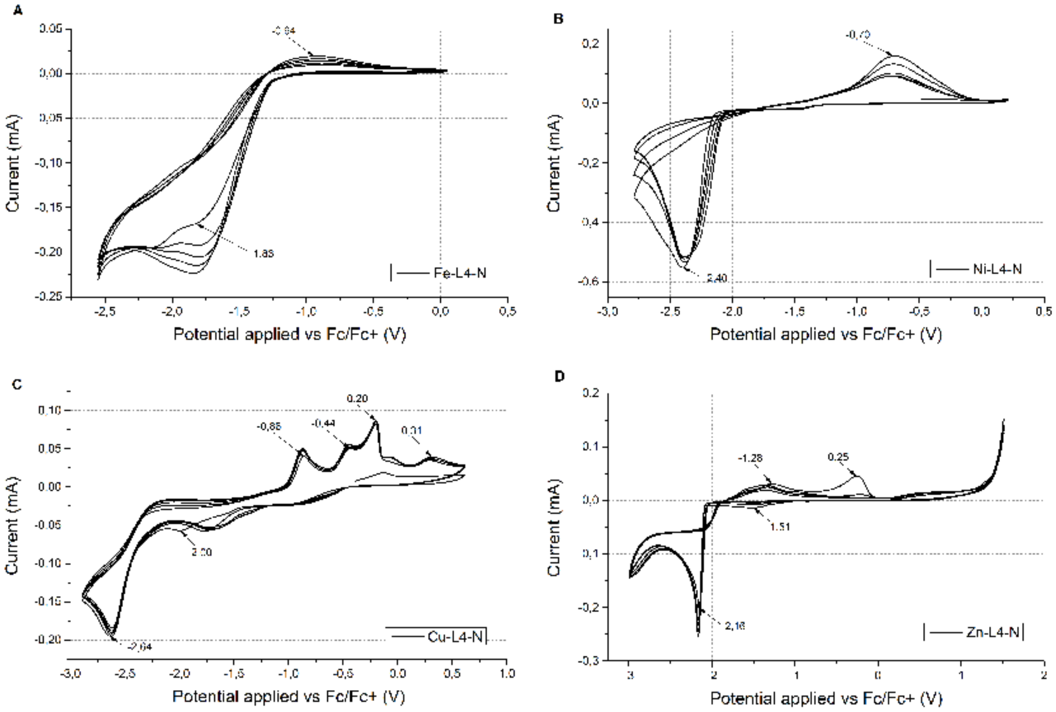

Figure 94: Voltammogram for ECCs containing tris(3-aminopropyl)amine and corresponding nitrate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

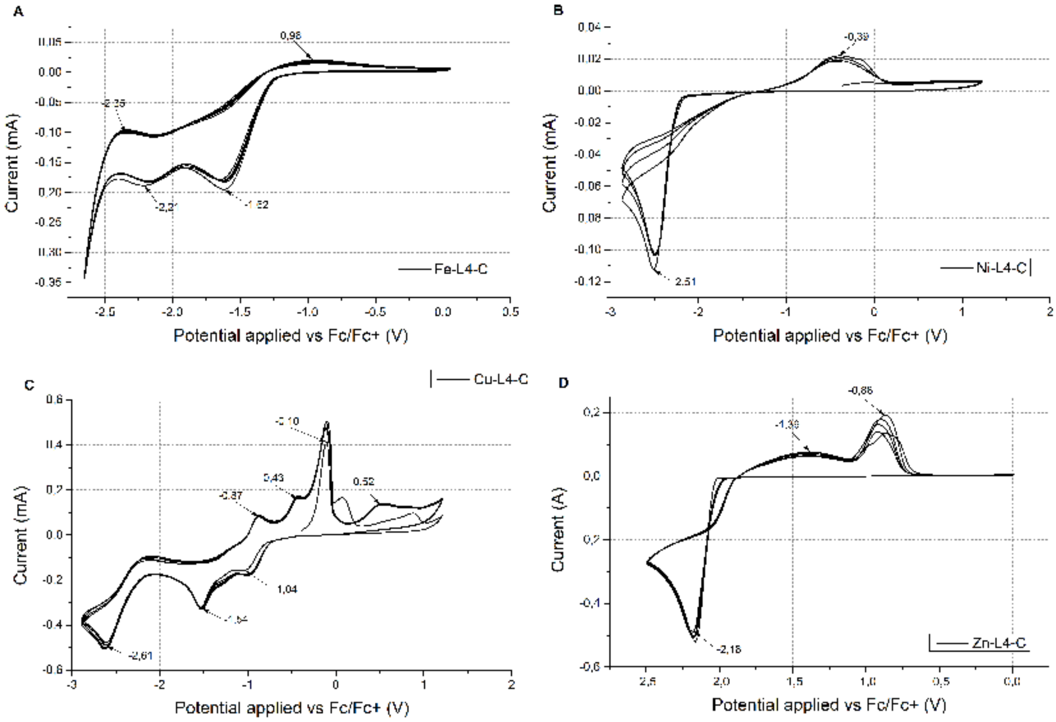

Figure 95: Voltammogram for ECCs containing tris(3-aminopropyl)amine and corresponding nitrate analogues: A - Fe; B - Ni; C - Cu; D - Zn.

Table 40: Oxidation and reduction potencial values for ECCs containing 1,3-diaminopropane.

Sample code	Oxidation potential [V]	Reduction potential [V]
Fe-L2-N	- 0.97	- 2.00
Ni-L2-N	- 0.20	+ 0.65
Cu-L2-N	- 0.91; - 0.19	- 2.02; - 1.26; -0.79
Zn-L2-N	- 1.81; - 1.53	- 2.27; - 1.93
Fe-L2-C	- 0.80	-
Ni-L2-C	- 0.64; + 0.02; + 0.76	- 2.10
Cu-L2-C	- 0.80; - 0.17	- 2.06; - 0.75
Zn-L2-C	- 1.78; - 1.24	- 2.04; - 1.80; -0.79

Table 41: Oxidation and reduction potencial values for ECCs containing tris(2-aminoethyl)amine.

Sample code	Oxidation potential [V]	Reduction potential [V]
Fe-L3-N	-	- 1.79
Ni-L3-N	- 0.03	- 2.70; - 2.35; - 1.50
Cu-L3-N	- 0.89; - 0.14; + 0.31	- 1.85
Zn-L3-N	- 1.58	- 2.39
Fe-L3-C	- 2.45	-1.64
Ni-L3-C	- 1.28; - 0.77	- 1.47; - 1.05
Cu-L3-C	- 0.83; - 0.19; - 0.10	- 1.65; - 1.23
Zn-L3-C	- 1.69; - 0.91	- 2.34; - 1.38

Table 42: Oxidation and reduction potencial values for ECCs containing tris(3-aminopropyl)amine.

Sample code	Oxidation potential [V]	Reduction potential [V]
Fe-L4-N	- 0.94	- 1.83
Ni-L4-N	- 0.70	- 2.40
Cu-L4-N	- 0.86; - 0.44; - 0.20; + 0.31	- 2.64; - 2.00
Zn-L4-N	- 1.28; - 0.25	- 2.16; -1.51
Fe-L4-C	- 2.35; - 0.96	- 2.21; -1.62
Ni-L4-C	- 0.39	- 2.51
Cu-L4-C	- 0.87; - 0.43; - 0.10; + 0.52	- 2.61; - 1.54; - 1.04
Zn-L4-C	- 1.39; - 0.86	- 2.18

Sensitivity to mechanical stimuli

Table 43: Friction sensitivity values for obtained nitrate and perchlorate analogues of ECCs.

Sample code	**Upper limit of insensitivity [N]**	**Sample code**	**Upper limit of insensitivity [N]**
Fe-L1-N	84	Fe-L1-C	108
Ni-L1-N	128	Ni-L1-C	168
Cu-L1-N	112	Cu-L1-C	96
Zn-L1-N	80	Zn-L1-C	144
Fe-L2-N	108	Fe-L2-C	128
Ni-L2-N	64	Ni-L2-C	112
Cu-L2-N	80	Cu-L2-C	60
Zn-L2-N	96	Zn-L2-C	216
Fe-L3-N	96	Fe-L3-C	80
Ni-L3-N	168	Ni-L3-C	168
Cu-L3-N	108	Cu-L3-C	72
Zn-L3-N	192	Zn-L3-C	160
Fe-L4-N	60	Fe-L4-C	84
Ni-L4-N	89	Ni-L4-C	128
Cu-L4-N	144	Cu-L4-C	288
Zn-L4-N	84	Zn-L4-C	216

Table 44: Impact sensitivity values for obtained nitrate and perchlorate analogues of ECCs.

Sample code	**Upper limit of insensitivity [N]**	**Sample code**	**Upper limit of insensitivity [N]**
Fe-L1-N	> 50	Fe-L1-C	> 50
Ni-L1-N	10	Ni-L1-C	3
Cu-L1-N	> 35	Cu-L1-C	< 1
Zn-L1-N	40	Zn-L1-C	2
Fe-L2-N	10	Fe-L2-C	2
Ni-L2-N	20	Ni-L2-C	5
Cu-L2-N	35	Cu-L2-C	7.5
Zn-L2-N	25	Zn-L2-C	5
Fe-L3-N	> 50	Fe-L3-C	3
Ni-L3-N	> 50	Ni-L3-C	5
Cu-L3-N	> 50	Cu-L3-C	< 1
Zn-L3-N	40	Zn-L3-C	5
Fe-L4-N	> 50	Fe-L4-C	5
Ni-L4-N	> 50	Ni-L4-C	7.5
Cu-L4-N	> 50	Cu-L4-C	1
Zn-L4-N	> 50	Zn-L4-C	> 50