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Comparison of 1-Ethyl-5*H*-tetrazole and 1-Azidoethyl-5*H*-tetrazole as Ligands in Energetic Transition Metal Complexes

Maximilian H. H. Wurzenberger[a], Michael S. Gruhne[a], Marcus Lommel[a], Norbert Szimhardt[a], Thomas M. Klapötke[a], and Jörg Stierstorfer*[a]

Abstract: Energetic coordination compounds (ECC) based on 3d or 4d transition metals show promising characteristics to be used as potential replacements for highly toxic lead-containing primary explosives. Herein we report the synthesis of 12 new ECC based on 1-azidoethyl-5*H*-tetrazole (AET) or 1-ethyl-5*H*-tetrazole (1-ETZ) as nitrogen-rich ligands as well as various central metals (Cu^{2+}, Fe^{2+}, Zn^{2+}, Ag^{+}) and anions such as perchlorate and nitrate. The influence of the increased endothermicity by adding an additional azide group was studied by comparing analogous ECC based on AET and 1-ETZ. Furthermore, the compounds were extensively analyzed by XRD, IR, EA, solid-state UV/Vis, and DTA as well as their sensitivities toward impact and friction were determined with BAM standard techniques, together with their sensitivity against electrostatic discharge. The sensitivities were compared with the one toward ball drop impact measurements. Classical initiation tests (nitropenta filled detonators) and ignition by laser irradiation highly prove the potential use of the most promising compounds in lead-free initiation systems.

Introduction

Ever since the discovery of the azide anion by Curtius in 1890,[1] the ongoing azide chemistry has fascinated several generations of chemists. Today almost every single element from the periodic table has been combined to build up covalent and ionic azides. The combination of simple main-group and transition metals with the azide anion has provided one high point in this chemistry together with the well-deserved reputation for the explosive behavior.[2] Among easily available and industrial useful ionic azides, lead azide (LA) and sodium azide are the most prominent examples. Nowadays, NaN_3, as the cheapest azide source, is indispensable in many chemical transformations like substitutions or addition reactions in synthetic organic chemistry. Additionally, sodium azide was also found in previous airbag systems.[3] Covalently bonded and ionic azides, in particular, heavy metal azides, are known as thermally decomposable and, in part, explosive classes of compounds. LA is one of the most commonly used primary explosives in both industrial and military applications. However, alternatives, so-called green primary explosives, are in great demand to prevent the considerable, highly toxic lead contamination in military training grounds. Over 95 % of all missile launches, shooting, and explosions within the police forces or military are done exclusively for training purposes in "friendly" areas,[4] leading to an ongoing research for new and more eco-friendly energetic materials.[5–10]

Since the discovery of phenyl azide in 1864,[11] azido organic compounds have attracted the attention of chemists due to their unique characteristics. The initial postulation of Curtius and Hantzsch for the structural determination of organic azides suggested a cyclic 1*H*-triazirine structure. Later, however, this hypothesis was rapidly revised in favor of the linear structure (Chart 1).[1,12–14] The chemical diversity of many organic azides can be explained on the basis of the physicochemical properties by a consideration of the polar mesomeric structures.[15,16]

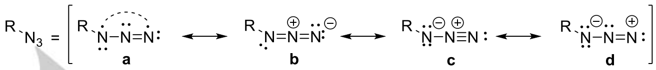

Chart 1. Mesomeric structures of covalent bonded azide.

The mesomeric structures **c** and **d**, proposed by Pauling,[17,18] compellingly explain the reactivity in 1,3-dipolar cycloadditions and the decomposition of azides to form nitrenes under the elimination of nitrogen gas. The reactivity of the azide functionality in terms of nucleophilicity (nucleophilic attack of N1) and electrophilicity (nucleophilic attack on N3) can be deduced from the basis of structure **d**. From a thermodynamic standpoint, the azide group is a structural fragment, which shows a high positive heat of formation and adding about 364 kJ mol^{-1} of endothermicity to a hydrocarbon compound.[19] Additionally, the azide groups exhibit an environmentally friendly balance, as nitrogen gas is produced as an exclusive smokeless combustion product. Therefore, organic azides are potential candidates for the use in high energetic materials like binders, hypergolic ionic liquids, plasticizers and additives (Chart 2).[2,20–23]

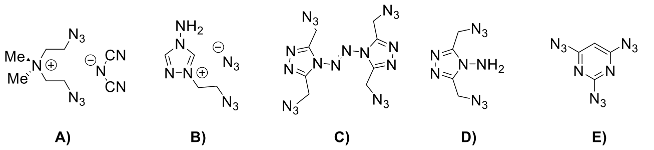

Chart 2. Representative examples for energetic organic compounds: hypergolic ionic liquids (bis(2-azidoethyl)dimethylammonium dicyanamide (**A**) and 1-(2-

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Supporting information, including X-ray data, IR spectra, DTA plots, column diagrams of the complexes, hot plate and hot needle tests, initiation capability tests, laser initiation tests, UV/Vis spectra, experimental part and general methods for this article is given via a link at the end of the document.

azidoethyl)-4-amino-1,2,4-triazolium azide (**B**)), energetic plasticizers (3,3',5,5'-tetra(azidomethyl)-4,4'-azo-1,2,4-triazole (**C**) and 4-amino-3,5-di(azidomethyl)-1,2,4-triazole (**D**)), or an energetic additive in nanotubes (2,4,6-triazidopyrimidine (**E**)).

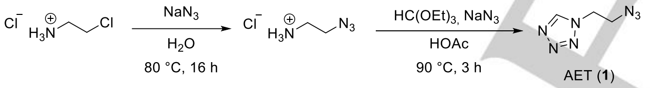
Due to the smokeless gas evolution, the major application nowadays is found in gas generators. Besides these utilizations of organic azides, the use in primary explosives is especially promising. Nitrogen-rich molecules are considered as prime candidates for "green" energetic materials[24–27] since the main combustion product is molecular dinitrogen and the materials exhibit desirable performance characteristics in high explosives (HE) due to their high positive heat of formation.

In this paper, we demonstrate the increasing performance of ECC by solely substituting one proton of the alkyl rest of 1-ethyl-5*H*-tetrazole with an azide group. The AET based transition metal complexes were both investigated toward their usability as lead-free primary and laser ignitable explosives. In addition, they were compared to their analogous ECC with unsubstituted 1-ETZ as nitrogen-rich ligand.

Results and Discussion

Synthesis

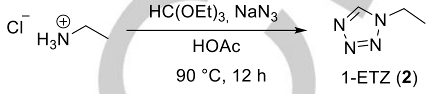
Over three decades ago, the synthesis of 1-azidoethyl-5*H*-tetrazole was published for the first time by Gaponik *et al.*.[28] The only reported complex is based on copper(II) chloride as metal salt and was only investigated for its crystal structure.[29] For synthesizing ligand **1** a two-step reaction, starting from a simple and cheap feedstock was performed (Scheme 1).



Scheme 1. Synthesis of 1-azidoethyl-5*H*-tetrazole (**1**) starting from 2-chloroethylamine hydrochloride.

The first target molecule was 2-azidoethylamine hydrochloride, which is less volatile than the neutral compound and for which several syntheses are already reported in literature.[30,31] 2-Chloroethylamine hydrochloride was reacted with sodium azide in water to form the intermediate in quantitative yield. The crude hydrochloride salt was converted in a [3+1+1] cyclization to the corresponding substituted alkyl tetrazole **1** by applying an excess of triethyl orthoformate and sodium azide in glacial acetic acid at elevated temperature. For the isolation of the nitrogen-rich ligand, the crude was filtrated, extracted with ethyl acetate and subjected to column chromatography leading to a yellowish oil in acceptable 33 % yield over two-steps. The physical state of **1** can be explained by previous reports showing the liquefying effect of the azidoethyl functionality.[2]

With 1-ethyl-5*H*-tetrazole (**2**), another ethyl-substituted 5*H*-tetrazole derivative is used for the synthesis of nitrogen-rich ECC in this work. The ligand can be obtained via the same selective pathway (Scheme 2) as mentioned above.[28] The [3+1+1] ring closure reaction again is performed, using triethyl orthoformate, sodium azide, and glacial acetic acid at 80 °C for 12 h. After filtration and extraction using ethyl acetate, the product was received in a satisfying yield of 75 %. Both tetrazole derivatives can easily be characterized by IR spectroscopy (Fig. S1), proton and carbon NMR spectroscopy. Additional, two dimensional ^1H, ^{15}N NMR HMBC or proton-coupled ^{15}N NMR spectroscopy can be performed (Fig. 1 and 2).



Scheme 2. Selective route for the synthesis of 1-ethyl-5*H*-tetrazole (**2**).

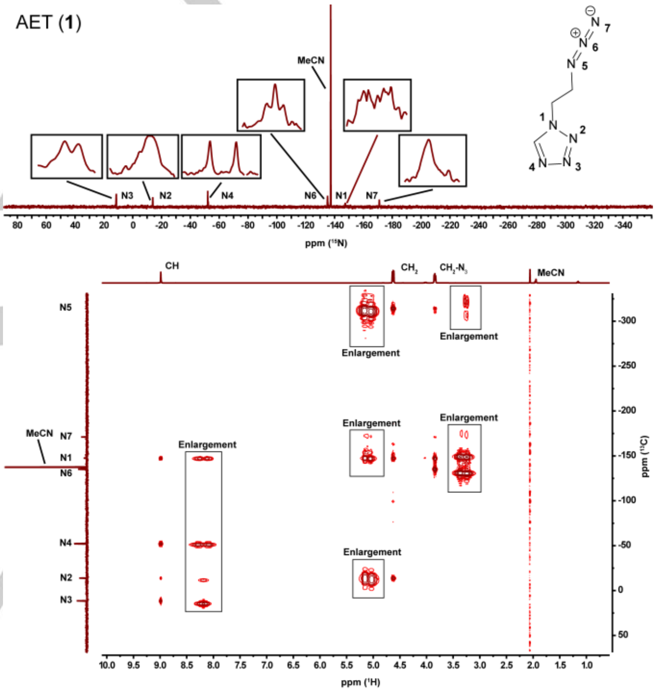


Figure 1. Proton coupled ^{15}N NMR spectra and two dimensional ^1H, ^{15}N-HMBC NMR spectra of **1**. ^{15}N NMR (MeCN-d_3, 25 °C, ppm) δ: 11.4 (N3, d, $^2J_{N\text{-}H}$ = 3.0), −13.9 (N2), −52.2 (N4, d, $^2J_{N\text{-}H}$ = 12.1 Hz), −135.2 (N6, t, $^2J_{N\text{-}H}$ = 3.3 Hz), −147.4 (N1, d, $^2J_{N\text{-}H}$ = 7.3 Hz), −171.1 (N7).

As mentioned, a large number of complexes based on various mono-tetrazoles (e.g. 1-methyl- or 1-amino-5*H*-tetrazole) have been described in literature, either having insufficient power or are way too sensitive for practical use.[32,33] In order to maximize the performance, ligand **1** is applied in the formation of new transition metal complexes, whereas the use of ligand **2** is a promising opportunity for reaching the middle course between both demands. The absence of acidic protons in both ligands allows their inclusion in neutral metal coordination compounds with oxidizing anions like nitrates, perchlorates, picrates (PA), styphnates (TNR) or 2,4,6-trinitro-3,5-dihydroxyphenolates (H_2TNPG). The selective integration of these anions in

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combination with one of the two ligands and different metal(I) or metal(II) cations, results in energetic coordination compounds with adjustable sensitivities and performance parameters. The formation of the coordination compounds **3**–**9** was achieved through the combination of ethanolic solutions of the relevant metal(I) or metal(II) salts and the ligand in stoichiometric amounts at r.t. or elevated temperatures in case of compound **3** (Scheme 3 and 4). Water and ethanol as solvent were chosen because of their non-toxic character and the good solubility of the ligand and the metal salts. Except coordination compound **3**, every complex crystallized without inclusion of water molecules. Complex **4** has only been obtained as a side species of **3**, making a further characterization impossible. Copper(II) chlorate complexes based on ligand **1** and **2** have been synthesized analogously to our recently published work (Scheme 5).[34]

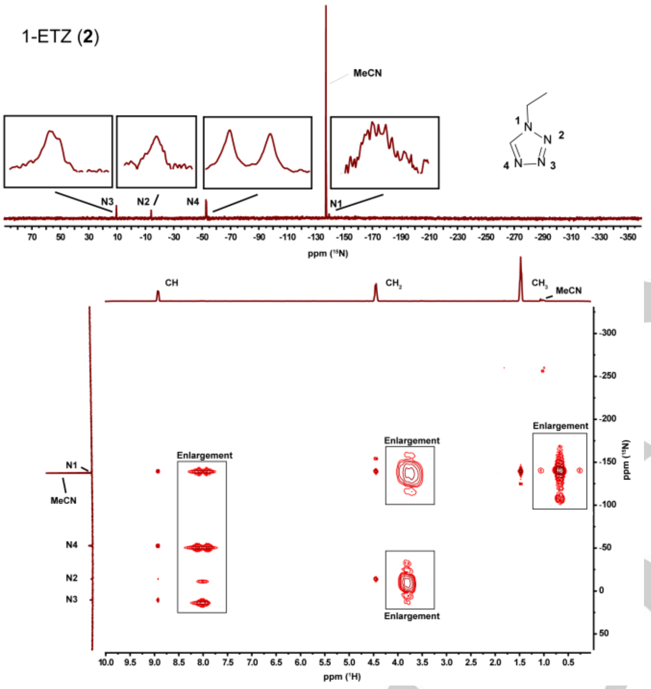
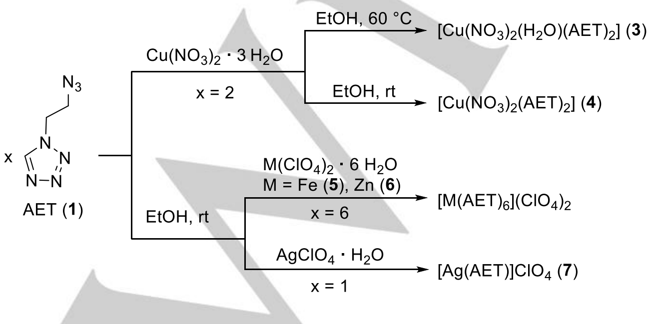
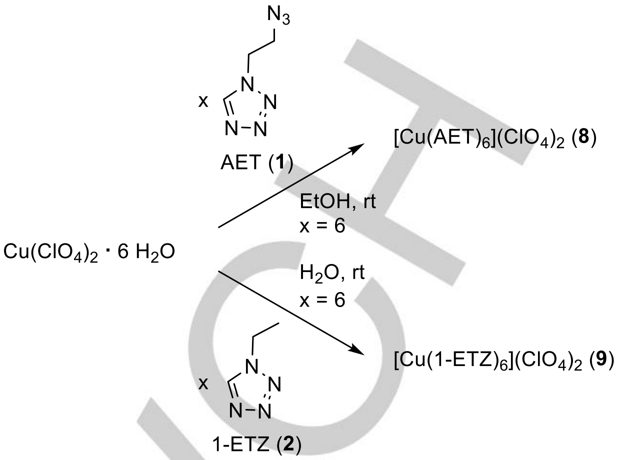


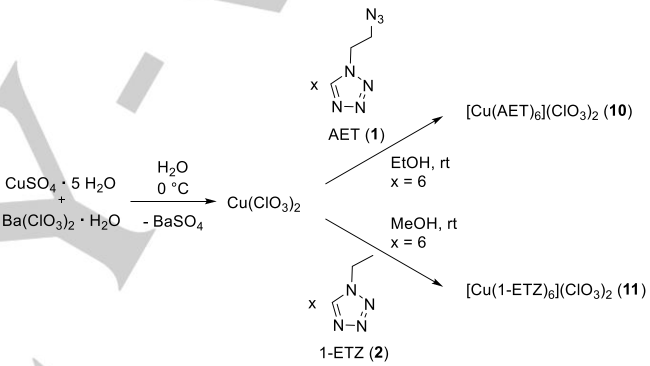
Figure 2. Proton coupled ^{15}N NMR spectra and two dimensional ^{1}H, ^{15}N-HMBC NMR spectra of **2**. ^{15}N NMR (MeCN-d_3, 25 °C, ppm) δ: 10.4 (N3), −14.1 (N2), −52.8 (N4, d, $^{2}J_{N\text{-}H}$ = 12.2 Hz), −139.5 (N1).



Scheme 3. Synthesis of the nitrato complexes **3** and **4** together with the perchlorate complexes **5**–**7**.

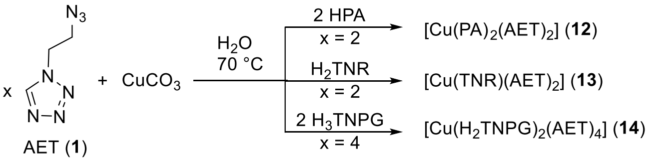


Scheme 4. Synthesis of the copper(II) perchlorate complexes **8** and **9**.



Scheme 5. Synthesis of the chlorate complexes **10** and **11**.

Due to the commercial unavailability of the copper(II) starting materials of the compounds **12**–**14**, an acid-base reaction had to be applied, starting from the respective 2,4,6-trinitrophenol derivatives and copper(II) carbonate in water at 70 °C. Filtration and treating with ligand **1** yielded the respective coordination compound (Scheme 6).



Scheme 6. Synthesis of the nitroaromatic coordination compounds **12**–**14**.

Potential precipitates during the addition of the ligand are dissolved by dropwise addition of water. Single crystals suitable for X-Ray diffraction were obtained directly from the mother liquor within a day. The filtration step after the acid-base reaction toward **12**–**14** turned out to be indispensable for elemental analysis pure

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products because traces of unreacted copper(II) carbonate cannot be removed by washing with cold ethanol after crystallization. All coordination compounds were obtained directly from the mother liquor and crystallized in satisfactory yields (38–87 %). The crystalline materials were filtered off, washed with small amounts of ice-cold ethanol and dried in air overnight. Single crystals suitable for X-ray diffraction of every compound except **5**, **8**, **9** and **10** were also obtained directly from the mother liquor. Crystals of the remaining coordination compounds were obtained after recrystallization from water.

Crystal Structures

The crystal structures of the ligands 1-azidoethyl-5*H*-tetrazole (**1**) and 1-ethyl-5*H*-tetrazole (**2**) are not described in literature. Due to their liquid state at r.t. and very low melting points, single crystals of those molecules were not obtained.

Therefore, single-crystal X-ray diffraction studies of all complexes were performed. Details on the crystal structures of compound **9** and **11** together with the measurement and refinement data of all complexes are given in the Supporting Information (Table S1–3 and Fig. S5–7). The crystal datasets were uploaded to the CSD database[35] and can be obtained free of charge with the CCDC no. 1898402 (**3**), 1898401 (**4**), 1898397 (**5**), 1898400 (**7**), 1898399 (**9**), 1898541 (**11**), 1898395 (**12**), 1898398 (**13**), 1898396 (**14**). All metal(II) (per)chlorate complexes show octahedral coordination spheres around the central metals built up by six molecules of ligand **1** or **2** (Fig. 4, S5 and S6). Unfortunately, compound **6**, **8** and **10** could only be measured at r.t. and are therefore highly disordered. Finalization of the datasets was impossible but the measurements allowed an insight into the complexes' composition, which were confirmed by elemental analysis and IR spectroscopy (Fig. S2–4). In all complexes, except compound **7**, both tetrazole derivatives coordinate to the central metals exclusively through their heterocyclic N4 nitrogen atoms. ECC **3** shows a rather uncommon sevenfold-bonded copper(II) cation (Fig. 3) and complex **7,** with Ag–N bond lengths between 2.323(3) and 2.538(3) Å, possesses distorted tetrahedrally coordinated silver ions.

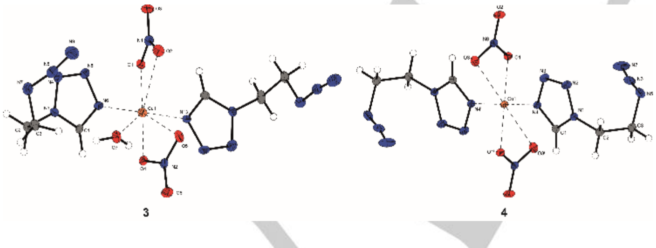

Figure 3. Molecular units of $[Cu(NO_3)_2(H_2O)(AET)_2]$ (**3**) and $[Cu(NO_3)_2(AET)_2]$ (**4**). Selected bond lengths (Å) of **3**: Cu1–N6 1.997(5), Cu1–N13 1.981(5); selected bond angles (°) of **3**: O1–Cu1–O2 52.15(15), O1–Cu1–O4 178.70(16), O1–Cu1–O5 127.78(15), O1–Cu1–N6 91.55(19), O1–Cu1–N13 88.86(19), O2–Cu1–O4 127.13(15), O2–Cu1–O5 78.29(14), O4–Cu1–O5 51.98(15), O4–Cu1–N13 92.32(19), O5–Cu1–O7 137.21(17), O5–Cu1–N6 98.24(17), O5–Cu1-N13 79.86(17), O7–Cu1–N6 92.5(2), O7–Cu1–N13 89.6(2), N6–Cu1–N13 177.85(19). Selected bond lengths (Å) of **4**: Cu–O1 1.9837(14), Cu1–O3 2.6497(18), Cu1–N4 1.971(2); selected bond angles (°) of **4**: O1–Cu1–O3 53.54(6), O1–Cu1–N4 89.96(7), O1–Cu1–O1^i 180.00, O1–Cu1–O3^i 126.46(6); symmetry code of **4**: (i) 1−x, 2−y, 1−z.

The copper(II) nitrato complex (**3**) crystallizes in the form of blue plates in the triclinic space group *P*–1 with two formula units per unit cell and a calculated density of 1.834 g cm^{-3} at 143 K. The sevenfold coordination environment of the copper(II) center consists of two chelating nitrato, one aqua, and two AET ligands. The nitrates are functioning as bidentate nitrato-ligands, resulting in a longer (2.734 Å) and a shorter (1.971 Å) Cu–O bond. Overall, the unusual amount of five ligands together with the extended sevenfolded coordination sphere results in three clearly longer Cu–O bonds (O2–Cu1 2.734(5) Å, O5–Cu1 2.734(5) Å O7–Cu1 2.337(5) Å), including the aqua ligand. The anhydrous nitrato complex **4** crystallizes in the form of blue blocks in the monoclinic space group $P2_1/c$ with two formula units per unit cell. The calculated density is 1.895 g cm^{-3} at 173 K. The closed octahedral coordination sphere again includes two chelating nitrato and two AET ligands (Fig. 3). The nitrato ligands are located in the equatorial and axial positions, whereas ligand **1** exclusively occupies equatorial positions. In consequence of the bidentate character of the nitrate, the bond angles are highly distorted from the ideal bond angle of 90°. A comparison of the complexes **3** and **4** shows, that the addition of a water ligand leads to a simple extension of the coordination sphere from a sixfold highly symmetric complex to a sevenfolded coordinated complex without any symmetry. In case of an extended coordination sphere, it is not surprising that in complex **4** the bond distances between the coordinating ligands and the copper(II) center are longer than the bond distances reported for the water-free compound **3**. Additionally, the torsion angle between the oxygens of one nitrate ligand is shortened from 53.54° (**4**) to 52.15° (**3**). The formation of a sevenfolded coordination sphere is a behavior, already observed for 1*H*-substituted tetrazole derivatives in copper(II) nitrato complexes with similar bond lengths around the central metal.[33]

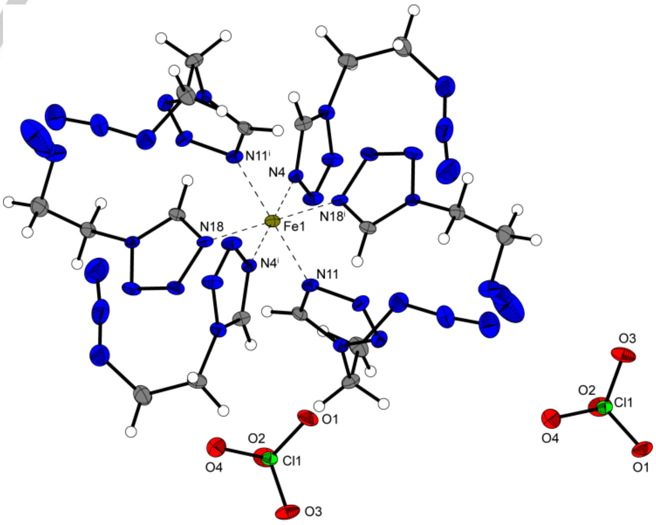

Figure 4. Molecular unit of $[Fe(AET)_6](ClO_4)_2$ (**5**). Selected bond lengths (Å): Fe1–N4 1.990(4), Fe1–N11 1.996(4), Fe–N18 1.977(5); selected bond angles (°): N11–Fe1–N11^i 180.00, N4–Fe1–N11 89.17(16), N18–Fe1–N18^i 180.00, N4–Fe1–N18^i 89.96(16), N4–Fe1–N4^i 180.00, N11–Fe1–N18 89.41(18); symmetry code: −x, −y, −z.

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The metal(II) perchlorate complexes **5**, **6** and **8** all crystallize isotypically in the monoclinic space group $P2_1/c$ with similar cell parameters and densities. Unfortunately, compounds **6** and **8** could only be measured at r.t. and therefore the ethyl azide moieties are highly disordered. The unit cell of **5** is built up by two formula units and possesses a calculated density of 1.648 g cm^{-3} at 128 K. The iron(II) central atom is surrounded by six molecules of ligand **1** (Fig. 4) with similar Fe1–N bond lengths. Both perchlorate anions are non-coordinating. The silver(I) complex **7** crystallizes in the form of colorless needles in the triclinic space group P–1 and consists of two formula units per unit cell. With a calculated density of 2.470 g cm^{-3} at 173 K, the complex possesses the highest one of all compounds (Fig. 5). In contrast to all other complexes based on AET, the ligand coordinates with four different coordination sides, in particular, the nitrogen atoms N2, N3, N4, and N5. This is resulting in the formation of one-dimensional polymeric chains (Fig. 6). For the first time, the azide functionality of the ligand **1** is involved in the coordination bonding, with an astonishing long bond of Ag1–N5 (2.538 Å). With its bond angles (N3^{ii}–Ag–N4^{i} = 122.84°, N2–Ag1–N5 = 77.31°), the tetrahedral formed by compound **7** strongly differs from the perfect angles of 109.47°. This deviation can be explained by the perchlorate anions located above and underneath the layers of silver ions and their interaction with these.

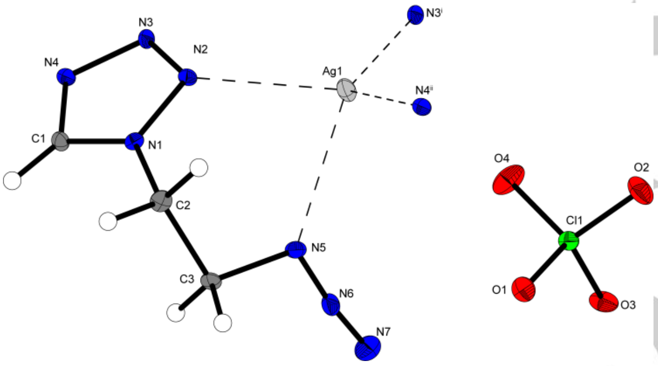

Figure 5. Coordination environment of [Ag(AET)](ClO$_4$) (**7**). Selected bond lengths (Å): Ag1–N2 2.420(3), Ag1–N4^{i} 2.323(3), Ag1–N3^{ii} 2.331(3); selected bond angles (°): N2–Ag1–N4^{i} 122.84(10), N2–Ag1–N3^{ii} 111.68(11), N4^{i}–Ag1–N5 86.06(11), N3^{ii}–Ag1–N5 133.85(10); symmetry codes: (i) −x, 1−y,1−z; (ii) 1+x, y, z.

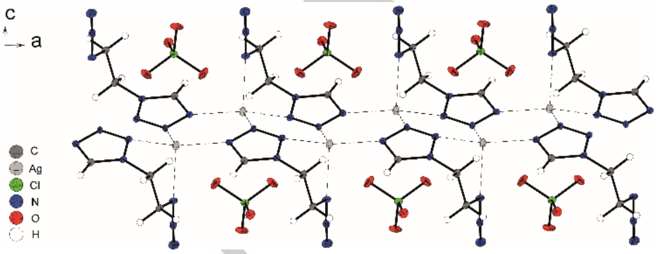

Figure 6. Segment of the polymeric chain of **7**, formed by tetrazole rings linking between three different silver atoms.

The coordination compound **12** crystallizes in the form of green plates in the monoclinic space group $P2_1/c$ with two formula units per unit cell. The complex possesses a calculated density of 1.815 g cm^{-3} at 143 K. The coordination sphere is built up by two equatorial arranged AET ligands and two molecules of picrate (Fig. 7). The anions are acting as bidental ligands, coordinating over the deprotonated hydroxy group and by another oxygen atom of one of the nitro groups. The latter occupy axial positions leading to a typical Jahn-Teller distortion along the O2–Cu1–O2^{i} axis.

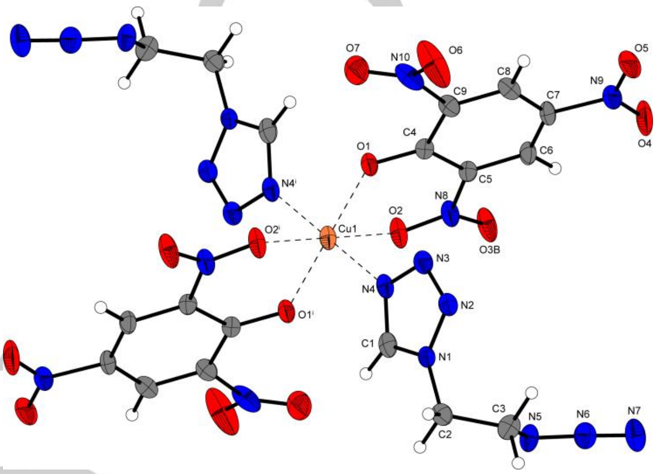

Figure 7. Molecular unit of [Cu(PA)$_2$(AET)$_2$] (**12**). Selected bond lengths (Å): Cu1–O1 1.931(4), Cu1–O2 2.334(3), Cu1–N4 1.997(4); selected bond angles (°): O1–Cu1–O1^{i} 180.00, O1–Cu1–O2 79.35(14), O1–Cu1–N4 91.62(17); symmetry code: (i) −x, 1−y, −z.

The styphnate complex **13** shows a similar density (1.803 g cm^{-3} at 143 K) to compound **12** and crystallizes in the triclinic space group P−1 with two formula units per unit cell (Fig. 8).

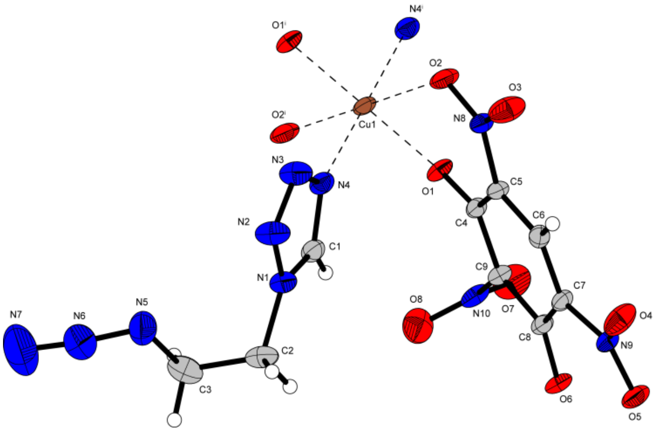

Figure 8. Coordination environment of [Cu(TNR)(AET)$_2$] (**13**). Selected bond lengths (Å): Cu1–O1 1.9266(16), Cu1–O2 2.3431(17), Cu1–N4 2.0115(19); selected bond angles (°): O1–Cu1–O1^{i} 180.00, O1–Cu1–O2 80.65(7), O1–Cu1–N4 88.92(7); symmetry code: (i) 2−x, −y, 2−z.

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Both hydroxy groups of styphnic acid are deprotonated leading to the formation of a trinitroresorcinate anion, which is coordinating to two different copper(II) cations by chelating each with one nitro and one phenolate oxygen. The Jahn-Teller-distortion along the O2–Cu1–O2^{i} is formed by two weaker bonded nitro groups of two different anions. Similar to silver complex **7**, **13** forms one-dimensional polymeric chains, which are however not caused by bridging ligands but by the fourfold coordinating anion (Figure S7). Coordination compound **14** crystallizes in the triclinic space group *P*−1 with only one formula unit per unit cell and a calculated density of 1.766 g cm^{-3} at 143 K. In contrast to nitroaromatic compound **13**, the anions are only single deprotonated and solely coordinating with the phenolate group (Fig. 9). The remaining equatorial positions are occupied by four instead of two molecules of ligand **1**. Again, the Jahn-Teller-distortion can be observed along the O–Cu–O axis.

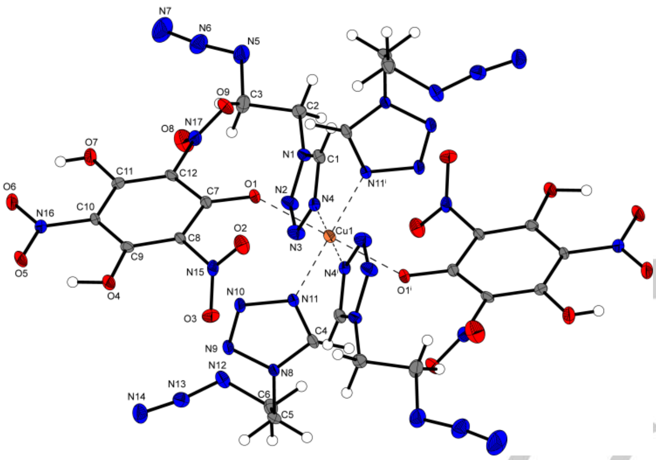

Figure 9. Unit cell of coordination compound [Cu(H$_2$TNPG)$_2$(AET)$_4$] (**14**). Selected bond lengths (Å): Cu1–O1 2.345(2), Cu1–N4 2.027(3), Cu1–N11 1.983(3); selected bond angles (°): O1–Cu1–N4 89.97(11), O1–Cu1–N11 95.31(11), O1–Cu1–O1^{i} 180.00, N4–Cu1–N11 89.59(11); symmetry code: (i) 1−x, −y, 1−z.

Sensitivities and thermal stability

The behavior of all compounds, except the side-product **4**, was investigated in differential thermal analysis (DTA). The measurements were performed in the range from 25–400 °C at a heating rate of β = 5 °C min^{-1}. Critical points are given as onset temperatures. The observed endothermic events (melting, dehydration or loss of coordinating ligand), as well as exothermic events, are listed in Table 1. DTA-plots of the compounds **1**–**3** and **5**–**14** are available in Fig. S12–15 in the SI.

The exothermic decomposition temperature reported for ligand **1** is in accordance with our findings, whereas for ligand **2** no data is available.[28] The exothermic decomposition temperatures of most of the investigated compounds are above 150 °C, except **10** ($T_{exo.}$ = 146 °C) and **14** ($T_{exo.}$ = 121 °C). The relatively low thermal stabilities of the nitrato compound **3** ($T_{exo.}$ = 152 °C), as well as the chlorate complexes, are a known issue, resulting from the metal salt, the coordination compounds are based on and is already reported in literature.[32,33] Besides its low point of exothermic decomposition, the nitrato complex (**3**) is the only compound showing two endothermic signals (T_{endo1} = 94 °C, T_{endo2} = 121 °C), indicating melting, followed by the loss of coordinating aqua ligand (proofed by TGA). Other endothermic events of compounds **6** and **8**-**11** can also be assigned to their respective melting points, which were also observed during heating of the respective compounds in hot plate tests. In order to examine the endothermic events more closely, some of the compounds were further investigated by thermal gravimetric analysis (Fig. S15). Except **3**, none of the compounds based on ligand **1** showed significant loss of mass until their exothermic decomposition points. Copper(II) complexes comprising 1-ETZ (**2**) show similar to the methyl-substituted analogous compounds evaporation of the ligand before their exothermic decomposition.[32] In the row of 2,4,6-trinitroaromatic based copper(II) complexes, the thermal stability decreases with increasing number of hydroxy groups, with **14** (T_{exo} = 121 °C) showing the lowest stability of all investigated compounds.

The highest exothermic decomposition temperature was observed for the copper(II) perchlorate complex **9** (T_{exo} = 210 °C), based on ligand **2**, showing an exothermic signal 52 °C higher than the analogous coordination compound based on ligand **1** (**8**: T_{exo} = 158 °C). The same can be observed for the two comparable chlorate complexes (Fig. 10). This trend is confirmed, looking at the temperatures evaluated for the respective ligand (**1**: T_{exo} = 193 °C; **2**: T_{exo} = 208 °C) and is guessed to be caused by the azido function of ligand **1**.

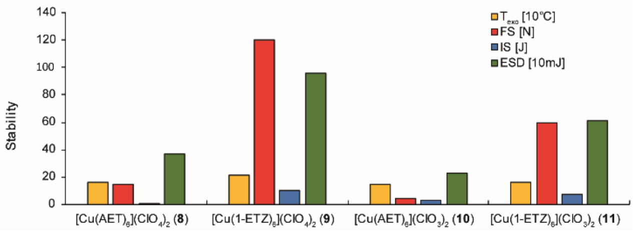

Figure 10. Comparison of the sensitivities and thermal stability of the chlorate and perchlorate complexes based on the ligands **1** and **2**, confirming the lower stability of chlorate compounds toward external stimuli.

A general trend within the row of the investigated 3d perchlorate coordination compounds shows higher exothermic decomposition temperatures with an increasing atomic number (Fe^{2+} < Cu^{2+} < Zn^{2+}), which is in conflict (Cu^{2+}-based complexes being less stable than Fe^{2+}) with our prior findings for 1*H*-substiuted tetrazoles (Fig 11).[32] Interestingly, compounds **6** and **9** even show slightly higher exothermic decomposition temperatures (T_{exo} = 196 °C and 210 °C, respectively) than the corresponding ligand.

The sensitivities toward impact (IS) and friction (FS) were assessed according to BAM standard methods (1 of 6) together with the electrostatic discharge sensitivity (ESD) for all compounds. In addition, all complexes have been categorized in accordance with the “UN Recommendations on the Transport of

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Dangerous Goods" using the determined sensitivities.[36] An overview of the sensitivities is given in Table 1. Because sensitivity data are highly affected by the crystal morphology, the compounds' grain size and habitus were investigated using light microscopy. The data are represented in the supplementary information (Fig. S8–11).

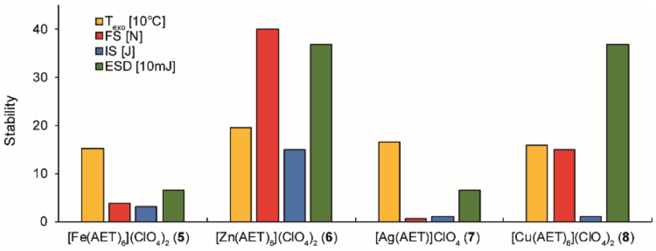

Figure 11. Comparison of the thermal stabilities together with the sensitivities toward various stimuli of the perchlorate coordination compounds **5**–**8**, showing that silver compound is the most sensitive and the zinc one is the most insensitive one.

The free ligand **2** is the only investigated compound to be ranked as insensitive with its high stability toward friction and impact. In contrast to that, ligand **1** has to be classified as sensitive because of its sensitivity of 9 J toward impact, whereas it is insensitive toward friction. No measurements regarding electrostatic discharge could be performed due to the physical state of both ligands. The highest stability toward impact of all ECC (15 J, sensitive) is possessed by the only zinc coordination compound **6**, which has to be considered as very sensitive because of its friction sensitivity. Comparing the perchlorate complexes reveals, that all have to be considered as very sensitive (**6**, **8**) or even extremely sensitive (**5**, **7**), except compound **9**, which is stated as sensitive, also possessing the highest stability toward friction of all investigated perchlorates. The sensitivity toward impact of the ECC based on perchlorate and AET increases in the following order: Zn^{2+} (15 J) < Fe^{2+} (3 J) < Cu^{2+} (<1 J) ≈ Ag^{+} (<1 J) and in the following order against friction: Zn^{2+} (40 N) < Cu^{2+} (15 N) < Fe^{2+} (3.75 N) < Ag^{+} (0.6 N) (Fig. 11). Again these results contradict earlier observations.[32,33]

Table 1. Overview of the compounds' thermal stability[a], sensitivities toward various external stimuli and results of hot plate (HP) and hot needle (HN) tests compared to lead azide.

Compound	$T_{endo.}$ (°C)[b]	$T_{exo.}$ (°C)[c]	IS[d] (J)	FS[e] (N)	ESD[f] (mJ)	BDIS[g] (mJ)	HP[h]	HN[h]
AET (**1**)	-	193	9	> 360	n.d.	n.d.	n.d.	n.d.
1-ETZ (**2**)	-	208	> 40	> 360	n.d.	n.d.	n.d.	n.d.
$[Cu(NO_3)_2(H_2O)(AET)_2]$ (**3**)	94, 121	152	10	108	840	n.d.	def.	def.
$[Fe(AET)_6](ClO_4)_2$ (**5**)	-	151	3	3.75	65-0	< 4	det.	det.
$[Zn(AET)_6](ClO_4)_2$ (**6**)	159	196	15	40	368	20	def.	def.
$[Ag(AET)]ClO_4$ (**7**)	-	165	< 1	0.6	65.0	< 4	det.	det.
$[Cu(AET)_6](ClO_4)_2$ (**8**)	135	158	< 1	15	368	12	def.	det.
$[Cu(1\text{-}ETZ)_6](ClO_4)_2$ (**9**)	172	210	10	120	960	n.d.	def.	def.
$[Cu(AET)_6](ClO_3)_2$ (**10**)	77	146	2.5	4	226	29	def.	det.
$[Cu(1\text{-}ETZ)_6](ClO_3)_2$ (**11**)	111	158	7	60	608	n.d.	def.	def.
$[Cu(PA)_2(AET)_2]$ (**12**)	-	183	3	252	226	> 200	def.	def.
$[Cu(TNR)(AET)_2]$ (**13**)	-	177	< 1	240	123	> 200	def.	def.
$[Cu(H_2TNPG)_2(AET)_4]$ (**14**)	-	121	1.5	84	608	> 200	def.	def.
$Pb(N_3)_2$[37]	-	320-360	2.5-4	0.1-1.0	7.00	n.d.	n.d	n.d

[a] Onset temperature at a heating rate of 5 °C min^{-1} measured by DTA; [b] Endothermic peak, which indicates melting, vaporization, dehydration, or loss of aqua ligands; [c] Exothermic peak, which indicates decomposition. [d] Impact sensitivity according to the BAM drophammer (method 1 of 6). [e] Friction sensitivity according to the BAM friction tester (method 1 of 6). [f] Electrostatic discharge sensitivity (OZM Electric Spark XSpark10). [g] Ball drop impact sensitivity determined with the 1 of 6 method in accordance with the MIL-STD 1751A (method 1016). [h] def.: deflagration; det.: detonation.

Compounds **8**–**11** show comparable trends to external stimuli as in thermal experiments. Complexes based on ligand **1** are more sensitive (**8** and **10** are both ranked as extremely sensitive) than those of compound **2** (both sensitive) and the copper(II) chlorate complexes are less stable (**11**) or at least show similar sensitivities (**10**) compared to the analogous perchlorate ones (Fig. 10), which is in accordance to our previous findings.[34] The nitroaromatic derivatives **12**–**14** possess one of the highest stabilities of all complexes toward friction, but due to their sensitivities toward impact, they are all ranked as very sensitive (Fig. S17).

Because of the realistic terms of testing, sensitivity toward ball drop impact (BDIS) was also determined for the most sensitive complexes **5**–**8**, and **10** (Fig. S18). Due to the high discrepancy of **12**–**14** regarding the sensitivities toward impact and friction according to BAM standard methods, ball drop experiments were carried out for those compounds too. In the case of the perchlorate complexes it becomes clear that low stability to friction (**7** < **5** < **8** < **6**) is accompanied by a higher sensitivity to BDIS (**7** ≈ **5** < **8** < **6**) and that the impact sensitivity in the drophammer experiments (**7** ≈ **8** < **5** <<< **6**) is less significant. The same trend can be observed for the nitroaromatic compounds **12**–**14**.

Primary explosive suitability evaluation and laser initiation

For an insight into the behavior toward fast heating with and without confinement and for gaining an overall insight in their applicability as a primary explosive hot plate and hot needle tests were performed for every investigated coordination compound (Table 1, Fig. 12 and S19–30). Except the chlorate and perchlorate complexes **5**, **7**, **8** and **10**, which at least showed detonations during one of the tests, every other compound only deflagrated.

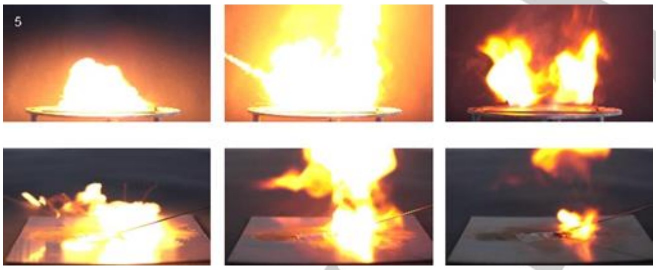

Figure 12. Hot plate test (top) and hot needle test (bottom) of the iron(II) perchlorate complex **5**, shown as a sequence.

The most promising compounds were tested in initiation capability tests with nitropenta (PETN) as the main charge. Further information on the test setup can be found in the General Methods of the Supporting Information. Positive tests, indicated by a hole in the copper witness plate and fragmentation of the shell, caused by a positive deflagration-to-detonation transition (DDT) toward the secondary explosive, were observed for **5** and **7**. $[Ag(AET)]ClO_4$ (**7**) is representing one of the rare ECC with silver as central metal being able to initiate PETN (Fig. 13). Tests concerning the copper(II) and zinc(II) perchlorate compound **6** and **8** did in our test not result in a positive DDT.

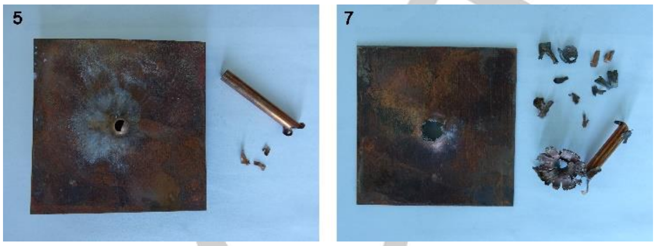

Figure 13. Positive results of the initiation capability tests toward PETN of compounds **5** and **7**.

Nowadays used primary explosives like LA or LS suffer, besides their toxicity, from their high sensitivity toward mechanical stimuli.[25] In classical initiation devices, which are based on mechanical stimuli, these properties are mandatory, but with the ability to be initiated by laser irradiation they are no longer required. This circumstance is responsible for the great interest that the field has gained in recent years.[38,39] Possible industrial applications like optical detonators or laser ignitable ammunition are already under current research.[40,41] Based on latest results concerning the laser ignition of ECC, this work focused only on the colored compounds **3**, **5** and **8**–**14**.[33] Further information for the applied setup can be found in the Supporting Information. All complexes showed reaction toward laser irradiation (Table 2), which strongly differed by the applied ligand and anion system.

Table 2. Results of the laser initiation experiments.[a]

Compound	0.17 mJ	25.5 mJ	30 mJ	111 mJ
3	—	—	deflag.	—
5	—	deflag.	det.	—
8	deflag.	det.	—	—
9	—	—	dec.	—
10	det.	det.	—	—
11	—	—	dec.	—
12	—	—	—	dec.
13	—	—	dec.	—
14	—	dec.	—	—

[a] (—: not tested, dec.: decomposition, deflag.: deflagration, det.: detonation). Operating parameters: current I = 7–12 A; voltage U = 4 V; theoretical maximal output power P_{max} = 45 W; theoretical energy E_{max} = 0.17–111 mJ; wavelength λ = 915 nm; pulse length τ = 0.1–20 ms.

As already recognized during hot plate and hot needle tests, coordination compounds based on the more energetic ligand **1** tend way more likely to show detonations than compounds based on ligand **2**. The use of nitrate or aromatic anions is leading to deflagrations only, whereas, in case of ligand **1**, the use of chlorates and perchlorates leads to detonations (Fig. 14 and S31–37).

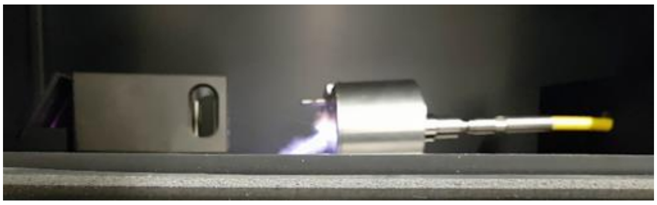

Figure 14. Detonation of the copper(II) perchlorate complex **8** during laser initiation test.

UV-Vis spectroscopy

Regarding the mechanism of laser initiation, UV-Vis spectra (Fig. S38 and S39) of all tested compounds were recorded in the solid-state and analyzed in detail at the laser operating wavelength of 915 nm. A summary of the optical properties of the measured compounds is given in Table S4. The observed absorption in the near infrared, visible and ultra-violet region results from the d-d transitions, based on the respective central metal and its interaction with the ligand and anion. Nevertheless, the process of initiation via laser irradiation (e.g. thermal, electrochemical) has still not been understood completely and is therefore of high importance and strongly investigated.[42,43] All complexes show moderate absorption behavior at the laser wavelength of 915 nm. This could be a possible explanation for the ignitability via laser irradiation since the colorless zinc and silver perchlorate compounds **6** and **7** could not be ignited. Besides the absorption in the desired area, other factors are important concerning laser initiation, like the corresponding metal or its electron configuration. Therefore, future studies should aim at the initiation process, in particular, the influence of the complexes' structure and the mechanism behind the initiation.

Conclusions

The nitrogen-rich ligands 1-azidoethyl-5*H*-tetrazole (**1**, AET) and 1-ethyl-5*H*-tetrazole (**2**, 1-ETZ), which can be synthesized in straight forward, green and cost-effective manners were successfully applied in coordination compounds and analyzed by two dimensional ^{1}H, ^{15}N HMBC NMR. Copper, iron, zinc, and silver salts of common anions like perchlorate or nitrate were used together with rather unusual ones like picrate, styphnate, trinitrophloroglucinate or chlorate. All of the synthesized coordination compounds, except byproduct **4**, were characterized in detail. By introducing the azide function into the ligand system, the performance of the ECC can be significantly increased. While the sensitivities of compounds **9** and **11** (based on 1-ETZ (**2**)) lie in the range of secondary explosives, most of the ECC based on ligand **1** are primary explosives. The iron (**5**) and silver (**7**) perchlorate compounds were both positive tested to initiate PETN, Especially compound **5** with its manageable sensitivities and nontoxic central metal could be a candidate of future interest. During laser ignition experiments coordination compound **5** as well as the copper compounds **8** and **10** showed detonations at energies between 0.17 mJ and 30.0 mJ making them promising candidates as green laser ignitable explosives. The comparison of the impact sensitivities determined by drophammer and ball drop reveals a higher similarity of the BDIS to FS than IS.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: energetic coordination compounds • tetrazoles • copper(II) • explosives • laser ignition

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[35] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code_(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: (deposit@ccdc.cam.ac.uk).

[36] Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N and > 80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.

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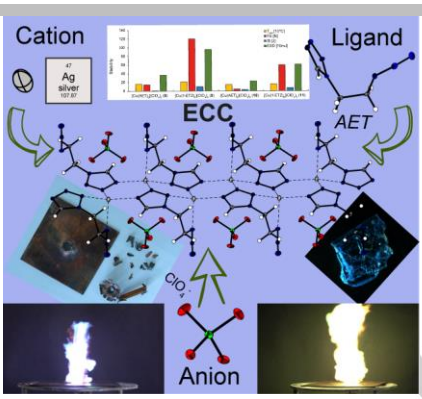
Entry for the Table of Contents

FULL PAPER

The performance of energetic coordination compounds (ECC) can be easily adjusted to the desired properties by varying one of their building blocks. In that study the substitution of one proton of 1-ethyltetrazole with an azide group and the comparison of the analog complexes by applying both ligands is discussed. ECC, consisting of the azide-ligand, show promising performances making them potential lead azide replacements.



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Comparison of 1-Ethyl-5*H*-tetrazole and 1-Azidoethyl-5*H*-tetrazole as Ligands in Energetic Transition Metal Complexes