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## Coordination chemistry with 1-methyl-5*H*-tetrazole: Cocrystallization, laser-ignition, lead-free primary explosives – One Ligand, three Goals

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The synthesis and characterization of 1-methyl-5*H*-tetrazole (**1**, MTZ) from 1,5*H*-tetrazole and methyl iodide is achieved. This neutral ligand was evaluated for its use in energetic transition metal complexes. The formation of complexes is a valuable concept because of the easy synthesis and the large number of possible combinations: i) metal, ii) ligand, and iii) anion. A series of 31 new complexes based on MTZ as the ligand was prepared in order to tune optical properties and sensitivity values by using seven different metals (Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>) and six different anions (chloride, nitrate, perchlorate, cyanodinitromethanide, picrate, styphnate). This variation allows to tailor the energetic properties of the desired molecule toward e.g. suitable primary explosives or laser-ignitable materials. Obtained compounds were characterized by low temperature single crystal X-ray diffraction, IR spectroscopy, elemental analysis and thermal analysis (DTA, DSC and TGA). The sensitivities toward external stimuli (impact, friction and electrostatic discharge) were determined according to the *Bundesamt für Materialforschung und -prüfung* (BAM) standard methods. These complexes have been characterized in laser ignition experiments and as new primary explosives. UV-Vis measurements of selected complexes were carried out to get a possible insight into the laser initiation mechanism. For the first time a large number of compounds with sensitivities ranging from insensitive to very sensitive were synthesized to give a wide range of new materials for different possible applications.

### Introduction

Lead styphnate and lead azide were put on the candidate list of authorization (substances of very high concern, Annex XIV) for the REACH (Registration, Evaluation, Authorization and Restriction of Chemicals)<sup>1</sup> regulations in 2011 due to their high toxicity. Almost certainly, the two compounds will be strictly regulated or banned. Therefore; research into possible leadfree replacements is strongly needed.

The use of endothermic ligands, such as tetrazoles and triazoles, in coordination compounds has been growing over the past few years with multiple uses in the field of inorganic chemistry.<sup>2,3</sup> Specifically, these complexes have applications as metal-organic frameworks (MOFs),<sup>4</sup> spin crossover systems<sup>5</sup> and energetic materials.<sup>6</sup>

Crystalline compounds containing two or more different species – including hydrates, solvates, coordinating and noncoordinating ligands – are defined as cocrystals and have an increasing number of applications as molecular semiconductors, advanced pharmaceuticals and optical materials.<sup>7</sup> In the field of energetic materials, cocrystallization can be used for enhancing the density and the detonation/combustion performance or to lower the mechanical sensitivities.<sup>8</sup> Regarding energetic complexes, this concept has recently been described with 1,2-di(1*H*-tetrazol-5-yl)ethane as the ligand.<sup>9</sup> In this work, the neutral ligand itself has been used as a cocrystallized species for the first time to increase the stability of the energetic complexes.

Coordination compounds of iron(II), in particular bearing alkylated tetrazole ligands like 1-methyl-5*H*-tetrazole (1), are one of the most investigated compounds in spin crossover systems.<sup>10</sup> The perchlorate and tetrafluoroborate iron(II) alkyltetrazole coordination compounds exhibited two different lattice sites for the central metals with a spin transition from high spin (*hs*) to low spin (*ls*) at a specific temperature.<sup>11</sup> Metastable long-lived *hs* and *ls* states on both sides can be induced through irradiation of green or red light, which makes spin crossover compounds interesting for uses in liquid crystals, gel phases and molecular switches.<sup>12</sup>

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<sup>&</sup>lt;sup>+</sup> Dedicated to John W. Fronabarger on the occasion of his 90<sup>th</sup> birthday. Parts of this work were presented at the 48<sup>th</sup> International Annual Conference 2017 of the Fraunhofer ICT in Karlsruhe (Germany)

Electronic Supplementary Information (ESI) available: X-ray Diffraction; IR spectroscopy of **3**, **6–10**, **17** and **23**; DTA plots of **1–10**, **12–14**, **27** and **29–37**; Thermal gravimetric analysis of **4**, **9**, **17** and **24**; Column diagrams of the complexes **15–26**; Hot plate and hot needle tests; Laser ignition tests; UV-Vis spectra of **15**, **20–27**, **31** and **36**, Experimental part. See DOI: 10.1039/X0xX00000x

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In terms of energetic materials, transition metal complexes have been proposed for numerous applications.<sup>13</sup> Ordinary used primary explosives, such as lead(II) azide, lead(II) styphnate and, in former times, mercury(II) fulminate (Chart 1), have led to significant contamination of the environment.<sup>14,15</sup> Energetic coordination compounds (ECCs) containing nitrogen-rich tetrazole ligands with high positive heats of formation and low or non-toxic metals like copper, zinc or iron can be used as substitutes for currently used primary explosives containing toxic heavy metals (Chart 2a/b).<sup>6,16,17,18</sup>



Chart 1 Commonly used primary explosives: lead(II) azide, lead(II) styphnate and mercury(II) fulminate.

The use of laser initiation systems is also becoming more attractive as a strategy for replacing sensitive primary explosives.<sup>19</sup> Instead of using very sensitive compounds for igniting secondary explosives, relatively insensitive energetic materials are ignited directly by laser irradiation. The ignition can be triggered by using high power lasers or with lower energies by adding small amounts of light absorbing materials to the energetic materials, like carbon black or chemical dyes.<sup>20</sup> However, promising explosive coordination complexes (ECCs), using transition metals as the central atom (for example Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> or Fe<sup>2+</sup>) and tetrazole ligands have been reported in literature that are ignitable by laser irradiation without the addition of dyes (Chart 2d).<sup>21,22</sup> The most prominent examples include pentaammine(5-cyano-2Htetrazolate)cobalt(III) perchlorate (CP)<sup>23</sup>, tetraammine-cisbis(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)cobalt(III) perchlorate (BNCP)<sup>24</sup> and 5-hydrazino-1H-tetrazolemercury(II) perchlorate (HTMP,  $(2c)^{25}$ . While they were initiated by laser ignition, they proved to be too sensitive for any application. The research of insensitive replacements is still of interest.



1-Methyl-5*H*-tetrazole (1) was first synthesized 1910 by reaction of methylisocyanide with hydrazoic acid by *Oliveri-Nandalá*.<sup>26</sup> The ligand has a high nitrogen content of 66.63 % and can be easily synthesized at low cost. The resulting driving force of producing nitrogen gas out of N–N single or N=N double bonds, makes it promising as a ligand in combination with oxidizing anions for ECCs. Until now, the compound has only been described in relation to EPR studies,<sup>27</sup> spin transition complexes<sup>10-12,28</sup>, and pyrotechnic<sup>29</sup>/propellant compositions.<sup>30</sup> Therefore, in this paper, efforts have been made to utilize MTZ as a neutral ligand to generate new energetic complexes with promising properties as (laser-ignitable) primary explosives or cocrystallized coordination compounds.

## **RESULTS AND DISCUSSION**

#### Synthesis

The nitrogen-rich heterocycle 1-methyl-5*H*-tetrazole (1, MTZ) can be synthesized in various ways. One route is the cycloaddition reaction of sodium azide with triethyl orthoformate and methylamine in acetic acid under reflux.<sup>31</sup> Another route is the nucleophilic methylation of 1H-tetrazole with a methylating agent such as methyl iodide. The methylation reaction reported here was carried out in acetone at 40 °C under reflux using potassium carbonate as base, according to a modified literature procedure (Scheme 1).<sup>32</sup> The methylation leads to an isomeric mixture of 1-methyl-5Htetrazole (1) and 2-methyl-5H-tetrazole. The desired product can be isolated from this mixture either by flash column chromatography or distillation. Filtration of the reaction mixture followed by distillation (MTZ: 90 °C, 0.01 mbar, 2-MTZ: 40 °C, 12 mbar) of the organic residue resulted in the isolation of the product 1 with a yield of 48 %. The side product 2methyl-5H-tetrazole was obtained with a yield of 23 %.



Scheme 1. Synthesis of 1-methyl-5*H*-tetrazole (1, MTZ).

The divalent transition metal complexes **2–13** and **15–26** were prepared by combining solutions of 1-methyl-5*H*-tetrazole (1) and metal(II) salts with the respective stoichiometries at room temperature (Scheme 2–4). Water was chosen as a nonflammable, low-volatile and cheap reaction medium because of the good solubility of both the metal(II) salts and the tetrazole ligand in this solvent. In order to get crystalline materials, a minimal amount of solvent was used. An iron(II) tetrachloridoferrate(III) coordination compound **2** with iron in two different oxidation states was synthesized analogous to the literature known spin crossover tetrabromidoferrate(II)

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complex of 1-methyl-5*H*-tetrazole.<sup>12</sup> Ethanol was used for recrystallization of **2** and as co-solvent in the synthesis of the perchlorate complexes **15–20** to get better crystallization. Complexes **4** and **5** have already been described in the literature and were synthesized to fill the gaps in the physico-chemical analytics.<sup>33,34</sup> The cobalt(II) and nickel(II) chlorido coordination compounds **6** and **7** crystallized, in contrast to **3– 5** and the literature reported CoCl<sub>2</sub>, NiCl<sub>2</sub> complexes, with four coordinating and two cocrystallized non-coordinating MTZ molecules. The nickel(II) chlorido complex **7** precipitated as a powder and single crystals could not be obtained by recrystallization. On comparison of the infrared spectra of **3**, **6** and **7**, and elemental analysis a complex formula of [NiCl<sub>2</sub>(MTZ)<sub>4</sub>] • 2 MTZ is proposed for the coordination compound **7** (Figure S20).



Scheme 2. Synthesis of the metal(II) chloride based MTZ complexes 2–7 with different metals centers.

The ligand has no acidic proton, which enables the integration of the neutral tetrazole ligand to assemble cationic or neutral complexes with oxidizing anions like nitrates, perchlorates, cyanodinitromethanides (CDNM), picrates (PA) or trinitroresorcinates (HTNR). The incorporation of these oxidizing anions leads to more sensitive and powerful energetic materials and are possible alternatives for lead free laser ignitable primary explosives.



Scheme 3. Synthesis of selected metal nitrate based MTZ complexes 8–13 with different metal centers.

Compound **11** lost the crystal water molecules and its crystallinity overnight, in contrast to **8–10**, and was analyzed in its anhydrous form **12**. The colored reaction mixtures were left

for crystallization until a precipitate appeared. The majority of the complexes were obtained in satisfying yields directly from the mother liquor as single crystals suitable for X-ray diffraction within a few hours or days. Unfortunately compound **14** precipitated as an amorphous powder in a low yield of **18**% and despite considerable recrystallization efforts single crystals could not be obtained.

The complex was synthesized by treatment of carbonatotetraaminecobalt(III) perchlorate with two equivalents of **1** in 15 % perchloric acid for 4 h. under reflux according to a modified procedure of an analogous compound.<sup>35</sup> The compound was filtered off, washed with a small amount of ethanol and dried in air.



Scheme 4. Synthesis of the energetic perchlorate coordination compounds 14–26.

All perchlorate complexes were obtained without inclusion of aqua ligands or water solvent molecules, which results in a higher performance. The synthesis of the perchlorate complexes is strongly dependent on the quantity of the ligand added and yields either a structure where all MTZ ligands are bound to the metal ions (15-20) or a complex unit with two additional cocrystallized tetrazoles (21-26) when an excess of the ligand is used. Both species can be clearly distinguished through infrared spectroscopy.<sup>32</sup> This is illustrated exemplarily for the cobalt(II) perchlorate complexes 17 and 23 in Figure S22. In addition to an intense stretching vibration around 1106 cm<sup>-1</sup> stemming from the perchlorate counter ions, a characteristic ring vibration of the bound MTZ ligand around 965  $\text{cm}^{-1}$  is observed in the spectra of both **17** and **23**. The free ligand as well as complex 23 exhibits a stretch in the spectra at around 997 cm<sup>-1</sup> stemming from in plane ring vibrations in free MTZ.<sup>32</sup> The C-H vibration can be detected at 3100 cm  $^{-1}$  in the free ligand and complex 23 spectra, respectively, while the bound MTZ ligand in 23 and 17 does occur at slightly higher wavenumbers  $(3147 \text{ cm}^{-1})$ .

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Formation of the complexes 27-32 with varying metal centers and Scheme 5. anions (CDNM= cyanodinitromethanide; HPA = picric acid, PA = picrate).

The corresponding metal(II) precursors for the complexes 27-37 were prepared and used in situ by simple acid-base reactions between metal(II) carbonates and picric/styphnic acid or metathesis reactions. The aqueous solutions of the corresponding precursors were then reacted with ligand 1 (Schemes 5 and 6). In some cases non-stoichiometric amounts of the ligand were used to increase the yield or purity of the respective compounds. All complexes crystallized within several minutes (copper(II) picrate and styphnate compounds) or days and were obtained directly from the mother liquor in reasonable yields (60-86 %). Crystals were filtered off, washed with cold ethanol when necessary to remove unreacted starting materials and dried in air, resulting in suitable samples for X-ray diffraction. Due to the high solubility of compound 33 in ethanol, no purification step was performed. In case of the manganese picrate complex 28 unfortunately only a few X-ray suitable single crystals could be picked between unreacted starting material and powder bulk material with unknown composition. The attempted synthesis of the coordination compound in sufficient amounts failed and only the crystal structure could be determined which is shown in the SI (Figure S12).



Scheme 6. Synthesis of the metal(II) based styphnate complexes 33-37.

#### **Crystal structures**

All complexes (except 4, 5, 7-9, 12, 14 and 16) were characterized using low temperature single crystal X-ray diffraction. Details on the crystal structures of complexes 3, 11, 15, 17, 18, 20, 21, 23-26, 28-30, 32 and 34-37 are given in the SI together with the measurement and refinement data. The single crystals of the cobalt(II) and nickel(II) nitrate complexes 8 and 9 were measured to give an indication of the most likely structures. Finalization of the data set was not possible because of the strongly disordered moieties and the related weak diffractions. The complexes 8 and 9 exhibit the same coordination environment and were therefore compared with 10 by infrared spectroscopy to confirm its structure (Figure S21). The crystal structures were uploaded to the CSD

database<sup>36</sup> and can be obtained free of charge with the CCDC nos. 1566368 (2), 1566362 (3), 1566371 (6), 1566381 (10), 1566384 (11), 1566379 (13), 1566370 (15), 1566366 (17), 1566363 (18), 1566364 (19), 1566361 (20), 1566359 (21), 1566380 (22), 1566382 (23), 1566385 (24), 1566386 (25), 1566360 (26), 1566378 (27), 1566377 (28), 1566376 (29), 1566372 (30), 1566375 (31), 1566383 (32), 1566373 (33), 1566367 (34), 1566374 (35), 1566365 (36), 1566369 (37). The bond lengths and angles of the coordinating and noncoordinating MTZ rings in the investigated complexes are in the typical range of tetrazole ligands and similar to the noncoordinating ligand 1.<sup>37,38</sup> The tetrazole ligand is therefore not discussed in detail in any of the following compounds. Coordination to the metal centers always takes place by the N4 nitrogen atom of 1-methyl-5H-tetrazole (1). All complexes with MTZ show an octahedral coordination sphere. This can be explained by the low steric hindrance of the ligand.

 $[Fe(MTZ)_6](FeCl_4)_2$  (2) contains iron in the oxidation states +II and +III. It crystallizes in the form of yellow blocks in the trigonal space group P-3 with one formula unit per unit cell and a calculated density of  $1.747 \,\mathrm{g \, cm}^{-3}$  at 123 K. The molecular unit consists of six asymmetric unit cells with a octahedrally coordinated iron(II) center, which is bonded to six MTZ ligands (Fe1–N1 = 2.010(13) Å, < (N1–Fe1–N1<sup>i</sup>) = 88.68(6)°). The second iron(III) atom is tetrahedrally coordinated by four chlorido-ligands (Fe2-Cl1 = 2.203(5) Å, <  $(Cl2-Fe2-Cl1^{vii}) = 109.49(2)^{\circ}, (Cl1^{vi}-Fe2-Cl1^{vii}) = 109.46(2)^{\circ})$ forming the tetrachloridoferrate(III) counteranion (Figure 1).



Figure 1 Molecular unit of [Fe(MTZ)<sub>6</sub>](FeCl<sub>4</sub>)<sub>2</sub> (2). Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50 % probability level. Selected bond lengths (Å): Fe1-N1 2.010(13), Fe2-Cl2 2.185(8), Fe2-Cl1 2.202(5); selected bond angles (°): N1-Fe1-N1<sup>i</sup> 88.68(6), N1-Fe1-N1<sup>ii</sup> 91.32(6), Cl2-Fe2-Cl1<sup>vi</sup> 109.49(2), Cl1<sup>vi</sup>-Fe2-Cl1<sup>vii</sup> 109.46(2). Symmetry codes: (i) y, -x+y, 1-z; (ii) -y, x-y, z; (iii) x-y, x, 1-z; (iv) -x+y, -x, z; (v) -x, -y, 1-z; (vi) -x+y, 1-x, z; (vii) 1-y, 1+x-y, z.

The cobalt(II) chlorido complex  $[CoCl_2(MTZ)_4] \bullet 2 MTZ$  (6) crystallizes in the form of yellow blocks in the monoclinic space group  $P2_1/c$  with two formula units per unit cell and a calculated density of 1.617 g cm<sup>-3</sup> at 123 K. In comparison to literature tetrazole containing complexes, most of the investigated compounds, show low densities, which can be attributed to the low density of MTZ itself.<sup>39</sup> The molecular unit contains two cocrystallized non-coordinating MTZ molecules, which are stabilized by non-covalent interactions and an octahedrally coordinated cobalt(II) cation. The metal(II) center is coordinated (Figure 2) by two chlorido ligands in axial

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**Figure 2** Molecular unit of [CoCl<sub>2</sub>(MTZ)<sub>4</sub>] • 2 MTZ (6). Selected bond lengths (Å): Co1– N1 2.143(6), Co1–N5 2.161(6), Co1–Cl1 2.443(2); selected bond angles (°): Cl1–Co1–N1 89.52(2), Cl1–Co1–N5 90.48(2), N1–Co1–N5 87.7(2). Symmetry code: (i) –x, 1–γ, –z.

The complexes **10** (colorless block) and **11** (blue block) with nitrate counterions are crystallizing isotypically in the triclinic space group P-1 with two formula units per unit cell showing almost the same metric (see Table S1 in the SI) and densities: **10**: 1.608 g cm<sup>-3</sup> and **11**: 1.626 g cm<sup>-3</sup> at 123 K.



Both metal(II) centers have an octahedral coordination sphere with six MTZ ligands (Figure 3 and S2). As expected, the  $d^9$ -ion

copper(II) ion in **11** shows Jahn-Teller distortion along its axial coordination sphere. In comparison, the respective zinc(II) complex exhibits a nearly undistorted coordination sphere and the six surrounding MTZ's is nearly undistorted (Zn1–N5 = 2.139(2) Å, Zn1–N1 = 2.166(2) Å, <  $(N5^{i}-Zn1-N9^{i}) = 88.23(8)^{\circ}$ , <  $(N1-Zn1-N9^{i}) = 89.51(8)^{\circ}$ ).

The silver(I) complex **13** crystallizes in the monoclinic space group  $P2_1/c$  with four formula units per unit cell and a calculated density of 2.112 g cm<sup>-3</sup> at 123 K. Every silver(I) center is penta-coordinated by two MTZ ligands and two bridging nitrates (Figure 4).



**Figure 4** Molecular unit of [AgNO<sub>3</sub>(MTZ]<sub>2</sub>] **(13**). The fifth ligand from an adjacent nitrate was omitted for clarity. Selected bond lengths (Å): Ag1–N1 2.233(3), Ag1–N5 2.255(3), Ag1–O1 2.544(3), Ag1–O3<sup>i</sup> 2.545(3), Ag1–O2 2.719(3), O1–N9 1.251(4), O2–N9 1.257(5), O3–N9 1.252(4); selected bond angles (°): N1–Ag1–N5 137.76(12), N1–Ag1–O1 111.85(11), N5–Ag1–O1 95.09(11), N1–Ag1–O3<sup>i</sup> 119.23(11), N5–Ag1–O3 95.82(11), O1–Ag1–O3<sup>i</sup> 81.30(10), O1–N9–O3 120.7(3), O1–N9–O2 119.6 (3), O3–N9–O2 119.7(3). Symmetry codes: (i) 1+x, y, z; (ii) –1+x, y, z.

The nitrato ligand binds through all of its three oxygen atoms. In addition to a bidentate coordination mode to one silver(I) cation, the nitrato ligand is also bound in a monodentate fashion to a second silver(I) ion, bridging the two cations and forming polymeric chains along the *a* axis (Figure 5). The distances between silver(I) and oxygen (Ag1–O1 = 2.544(3) Å, Ag1–O3<sup>i</sup> 2.545(3) Å, Ag1–O2 2.719(3) Å) are longer than the silver(I) nitrogen distances (Ag1–N1 = 2.233(3) Å, Ag1–N5 = 2.255(3) Å).



**Figure 5** View on the structure of **13** along the *a* axis (Ag–O bonds = cyar; Ag–N bonds = green). Stabilization through non-classical hydrogen bonds (C–H••N and C–H••O; C–H••O hydrogen bonds = purple) and hydrophobic interactions between the methyl groups.

The complexes with perchlorate counterions **15/20** and **17/18** crystallize isotypically in monoclinic and trigonal space groups (**15**:  $P2_1/n$ , 1.582 g cm<sup>-3</sup> (Figure S3); **17**: R-3, 1.614 g cm<sup>-3</sup> (Figure S4); **18**: R-3, 1.629 g cm<sup>-3</sup> (Figure S5); **20**:  $P2_1/n$ ,

1.635 g cm<sup>-3</sup> at 123 K (Figure S6)). The blue copper(II) perchlorate compound **19** is the only complex that crystallizes in the triclinic space group *P*-1 with two formula units per unit cell and a calculated density of 1.645 g cm<sup>-3</sup> at 123 K, which is the highest of all perchlorates. Its molecular motif is illustrated in Figure 6. Each metal(II) center contains an octahedral surrounding and is connected to six tetrazole ligands. As already observed in the coordination environment of the cation in **11**, the copper(II) center shows a Jahn-Teller distortion caused by the d<sup>9</sup>-configuration (Cu1–N1 2.035(2) Å, Cu1–N5 2.014(2) Å, Cu1–N9 2.401(2) Å).



Figure 6 Complex unit of  $[Cu(MTZ)_6](ClO_4)_2$  (19). Selected bond lengths (Å): Cu1–N1 2.035(2), Cu1–N5 2.014(2), Cu1–N9 2.401(2), Cl2–O5 1.437(2); selected bond angles (°): N1–Cu1–N5 89.83(2), N1–Cu1–N9 91.04(2), N5–Cu1–N9 89.54(2), O5–Cl2–O6 109.32(2). Symmetry codes: (i) –x, 2–y, –z; (ii) 1–x, –y, 1–z; (iii) 1–x, 1–y, 1–z; (iv) –x, 1–y, –z.

New perchlorate species **21–26** of the investigated metals(II) were obtained after using an excess of the tetrazole ligand during the synthesis. The complexes with two cocrystallized tetrazoles crystallize isotypically in the triclinic space group *P*–1 with one formula unit per unit cell and similar densities. However, their densities increase in the row of  $Mn^{2+}$  (1.590 g cm<sup>-3</sup>; 123 K) < Fe<sup>2+</sup> (1.592 g cm<sup>-3</sup>; 173 K) < Co<sup>2+</sup> (1.612 g cm<sup>-3</sup>, 143 K) < Ni<sup>2+</sup> (1.621 g cm<sup>-3</sup>; 143 K) < Cu<sup>2+</sup> (1.623 g cm<sup>-3</sup>; 143 K) < Zn<sup>2+</sup> (1.630 g cm<sup>-3</sup>; 123 K). The molecular structure of complex **22** is shown in Figure 7 and used exemplarily for all complexes.



Figure 7 Complex unit of  $[Fe(MTZ)_6](ClO_4)_2 \bullet 2 MTZ (22)$ . Selected bond lengths (Å): Fe1-N12 2.181(2), Fe1-N4 2.183(2), Fe1-N8 2.194(2), Cl1-O4 1.405(4); selected bond angles (°): N12-Fe1-N4 89.53(8), N12<sup>i</sup>-Fe1-N4 90.48(8), O1-Cl1-O4 108.1(2), N12-Fe1-N8<sup>i</sup> 91.61(8), N12<sup>i</sup>-Fe1-N8<sup>i</sup> 88.39(8), N4-Fe1-N8<sup>i</sup> 89.63(8), N4<sup>i</sup>-Fe1-N8<sup>i</sup> 90.37(8), N12<sup>i</sup>-Fe1-N8 91.61(8). Symmetry codes: (i) -x, -y, 1-z; (ii) 1-x, 1-y, -z; (iii) 1-x, 1-y, 1-z.

Again, two additional non-coordinating MTZ molecules could be cocrystallized. Six regular tetrazole ligands are surrounding the transition metal(II) centers in octahedral arrangements and interact hydrophobically and through non-classical hydrogen bonds with the cocrystallized compounds.

The cyanodinitromethanide complex **27** crystallizes in the form of blue blocks in the triclinic space group P-1 with one formula unit per unit cell and a calculated density of 1.746 g cm<sup>-3</sup> at 123 K.

The molecular unit is built up of two asymmetric unit cells. The octahedral complex (Figure 8), with four MTZ ligands in a plane (Cu1–N8 = 2.002(16) Å, Cu1–N1 = 2.019(19) Å, <  $(N8^{i}-Cu1-N7^{i})$  = 88.54(6)°, <  $(N1^{i}-Cu1-N7^{i})$  = 90.72(7)°), shows, elongation along the axial positions, which are occupied by two cyanodinitromethanide anions (Cu1–N7 = 2.412(18) Å). The structure of the CDNM anion is comparable to literature values.<sup>40</sup>



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Figure 8 Molecular unit of [Cu(CDNM)<sub>2</sub>(MTZ)<sub>4</sub>] (27). Selected bond lengths (Å): Cu1– N8 2.002(16), N6–C3 1.399(2), N7–C4 1.151(3), Cu1–N1 2.019(19), C3–C4 1.407(3), Cu1–N7 2.412(18), N5–C3 1.394(3), O2–N5 1.238 (2), O4–N6 1.243(3); selected bond angles (°): N8–Cu1–N1<sup>i</sup> 91.31(7), N8<sup>i</sup>–Cu1–N1<sup>i</sup> 88.69(7), N8–Cu1–N7<sup>i</sup> 91.46(6), N1<sup>i</sup>–Cu1– N7<sup>i</sup> 90.72(7), N1–Cu1–N7<sup>i</sup> 89.28(7), N8–Cu1–N7 88.54(6), O3–N6–O4 122.53(17), O3– N6–C3 122.02(18), O4–N6–C3 115.45(16), C1–N1–N2 106.45(18), N5–C3–N6 124.47(17), N5–C3–C4 117.23(16), N7–C4–C3 178.0(2). Symmetry code: (i) 1–x, –y, –z.

The manganese(II) 28 and cobalt(II) 29 picrate complexes crystallize isotypically in the monoclinic space group  $P2_1/c$  with two formula units per unit cell and calculated densities of  $1.746 \text{ g cm}^{-3}$  at 123 K for **28** and 1.786 g cm<sup>-3</sup> at 173 K for **29**. Their molecular units consist of two asymmetric units, containing one MTZ ligand, two aqua ligands, one crystal water and one non-coordinating picrate counteranion (Figure S12/13). The same monoclinic space group  $P2_1/c$  could be observed for the nickel(II) picrate complex **30** (1.757 g cm<sup>-3</sup> at 123 K), which shows a different molecular composition with no crystallized water molecules, two aqua and four MTZ ligands (Figure S14). Among the metal(II) picrate complexes, only the copper(II) 31 and zinc(II) 32 complexes crystallize water-free in monoclinic space groups (31:  $P2_1/c$ ; 32:  $P2_1/n$ ) with two formula units per unit cell and calculated densities of  $1.828 \text{ g cm}^{-3}$  at 123 K for **31** and 1.724 g cm $^{-3}$  at 173 K for **32**.



**Figure 9** Molecular unit of the copper(II) picrate complex **31**. Selected bond lengths (Å): Cu1–N4 2.001(3), Cu1–O4 2.354(2), Cu1–O7 1.929(2); selected bond angles (°): O4–Cu1–N4 91.63(9), O7–Cu1–N4 91.07(9), O4–Cu1–O7 79.32(9). Symmetry code: (i) 1–x, 1–y, –z.

In comparison to the other picrate compounds discussed so far, the trinitrophenolate counteranions coordinate bidentately to the copper(II) (via the nitro- and deprotonated phenolate-groups) and monodentately to the zinc(II) metal cations in **31/32**. The remaining coordination sites of the octahedron are occupied by two methyltetrazole ligands in **31** (Figure 9) and by four tetrazoles in **32** (Figure S15). The octahedral geometry of **31** shows deviations to the ideal 90° angle caused by the fixed structure of the picrate anion and its Jahn-Teller distortion along the O4–Cu1–O4<sup>i</sup> axis (< (O4–Cu1–N4) = 91.63(9)°, < (O7–Cu1–N4) = 91.07(9)°, < (O4–Cu1–O7) = 79.32(9)°).

The manganese(II) styphnate complex **33** interestingly crystallizes isotypically to the zinc(II) picrate complex **32** with

almost the same density  $(1.732 \text{ g cm}^{-3} \text{ at } 123 \text{ K})$  but with different anionic ligands, and is depicted in Figure 10.



Figure 10 Molecular unit of [Mn(HTNR)<sub>2</sub>(MTZ)<sub>4</sub>] (**33**). Selected bond lengths (Å): Mn1– O3 2.156(2), Mn1–N4 2.250(3), Mn1–N8 2.239(3); selected bond angles (°): O3–Mn1– N4 93.04(9), O1–Mn1–N8 85.42(11), N4–Mn1–N8 92.18(10). Symmetry code: (i) –x, 2–y, –z.

The cobalt(II) **34** and nickel(II) **35** styphnate complexes (Figures S16 and 17) crystallize isotypically to each other and to the picrate complexes **28/29**. A similar situation can be observed for complex **36**, which exhibits a similar coordination sphere like **31** with analogous cell parameters but with styphnates instead of picrates (Figure S18). The zinc(II) complex **37** has the same sum formula as compound **36**, but crystallizes triclinic in the space group *P*–1 and a different metal center (Figure S19).

#### Sensitivities and thermal stability

Thermal measurements of highly energetic and sensitive complexes are very challenging since larger quantities (> 2 mg) can damage the instrument seriously. On the other hand endothermic signals may not be detected properly when using an insufficient amount. Endothermic events like dehydration, melting or loss of cocrystallized/coordinating MTZ molecules, as well as other critical temperatures of the described compounds were measured with a heating rate of  $\beta$  = 5 °C min<sup>-1</sup> via differential thermal analysis, differential scanning calorimetry or by thermal gravimetric analysis. The measured onset temperatures are summarized in Tables 1 and 2. Details on the DTA plots of complexes 1-10, 12-14, 27 and 29-37 are given in the Supporting Information. Most of the complexes have exothermic decomposition events higher or close to 200 °C, which is in the range of the uncoordinated ligand 1 ( $T_{exo}$ : 206 °C). However, endothermic decompositions e.g. loss of water or ligand have been observed partly at lower temperatures. Both nitrate complexes 12 and 13, which decompose exothermically at relatively low temperatures of 160 °C (12) and 119 °C (13), showed the lowest thermal stabilities of all investigated compounds. Comparing them to the other coordination compounds bearing the same metal ion, but different anions, no general trend regarding their decomposition temperatures could be observed.

	<i>Т</i> <sub>епdo1.</sub> (°С) <sup>[а]</sup>	T <sub>endo2</sub> . (°C) <sup>[a]</sup>	<i>Т</i> <sub>ехо.</sub> (°С) <sup>[b]</sup>
MTZ (1)	39	_	206
[Fe(MTZ)6](FeCl4)2 (2)	_	_	236
[MnCl <sub>2</sub> (MTZ) <sub>2</sub> ] (3)	_	_	234
[CuCl <sub>2</sub> (MTZ) <sub>2</sub> ] (4)	185	_	199
[ZnCl <sub>2</sub> (MTZ) <sub>2</sub> ] (5)	184	_	204
[CoCl <sub>2</sub> (MTZ) <sub>4</sub> ] • 2 MTZ (6)	66	_	206
[NiCl <sub>2</sub> (MTZ) <sub>4</sub> ] • 2 MTZ (7)	106	_	199
[Co(MTZ) <sub>6</sub> ](NO <sub>3</sub> ) <sub>2</sub> • 2 H <sub>2</sub> O (8)	_	_	199
[Ni(MTZ)₀](NO₃)₂ • 2 H₂O (9)	86	166	194
[Zn(MTZ) <sub>6</sub> ](NO <sub>3</sub> ) <sub>2</sub> • 2 H <sub>2</sub> O (10)	50–75 <sup>[c]</sup>	_	196
[Cu(MTZ)₀](NO₃)₂ (12)	_	_	160
[AgNO₃(MTZ)₂] (13)	_	_	119
[Co(NH <sub>3</sub> ) <sub>4</sub> (MTZ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub> (14)	_	_	201
[Mn(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (15)	_	_	223
[Fe(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (16)	_	_	213
[Co(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (17)	—	_	253
[Ni(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (18)	_	_	271
[Cu(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (19)	178	_	211
[Zn(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (20)	196	_	221

Onset temperatures at a heating rate of 5 ° min<sup>-1</sup> [a] endothermic peak, which indicates melting, dehydration or loss of coordinating/cocrystallized MTZ molecules; [b] exothermic peak, which indicates decomposition; [c] weight loss detected by TGA.

Table 2.      Thermal stability measurements of 21–27 and 29–37 by DTA.				
	<b>T</b> <sub>endo1</sub> . (°C) <sup>[a]</sup>	<b>T</b> <sub>endo2.</sub> (°C) <sup>[a]</sup>	<i>Т</i> <sub>ехо.</sub> (°С) <sup>[b]</sup>	
[Mn(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> • 2 MTZ (21)	105	_	216	
[Fe(MTZ)6](ClO4)2 • 2 MTZ (22)	111	_	215	
[Co(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> • 2 MTZ (23)	107	_	210	
[Ni(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> • 2 MTZ (24)	93	_	207	
[Cu(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> • 2 MTZ (25)	78	_	206	
[Zn(MTZ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> • 2 MTZ (26)	108	_	212	
[Cu(CDNM)2(MTZ)4] (27)	—	_	201	
[Co(H <sub>2</sub> O) <sub>4</sub> (MTZ) <sub>2</sub> ](PA) <sub>2</sub> • 2 H <sub>2</sub> O (29)	61 <sup>[c]</sup>	79 <sup>[c]</sup>	248	
[Ni(H <sub>2</sub> O) <sub>4</sub> (MTZ) <sub>2</sub> ](PA) <sub>2</sub> (30)	106	_	211	
[Cu(PA) <sub>2</sub> (MTZ) <sub>2</sub> ] (31)	_	_	226	
[Zn(PA) <sub>2</sub> (MTZ) <sub>4</sub> ] (32)	92	_	212	
[Mn(HTNR)₂(MTZ)₄] (33)	141	_	202	
[Co(H <sub>2</sub> O) <sub>4</sub> (MTZ) <sub>2</sub> ](HTNR) <sub>2</sub> • 2 H <sub>2</sub> O (34	<b>4)</b> 70	80	200	
[Ni(H <sub>2</sub> O) <sub>4</sub> (MTZ) <sub>2</sub> ](HTNR) <sub>2</sub> • 2 H <sub>2</sub> O (35	<b>5)</b> 86	105	227	
[Cu(HTNR) <sub>2</sub> (MTZ) <sub>2</sub> ] (36)	—	_	231	
[Zn(HTNR) <sub>2</sub> (MTZ) <sub>2</sub> ] (37)	-	—	214	

Onset temperatures at a heating rate of 5 ° min<sup>-1</sup> [a] endothermic peak, which indicates melting, dehydration or loss of coordinating/cocrystallized MTZ molecules; [b] exothermic peak, which indicates decomposition; [c] measured by DSC.

Exceptional endothermic events during the DTA measurements could be observed for the complexes (4, 5, 9, 19, 20, 32, 33) and were further investigated by thermal gravimetric analysis (Figure 11 and Figure S27). The free ligand 1, which has a relatively low melting point of 39 °C, shows a continuous weight loss at elevated temperatures until its exothermic decomposition temperature is reached. This fact can be attributed to its high vapour pressure and could be a

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possible explanation for the observed endothermic peaks in the DTA plots for the above-mentioned complexes. Comparable phenomena have been reported in the literature.<sup>41,42</sup> The endothermic loss of two coordinating MTZ molecules in the complexes 19 and 32 leads most likely to an intermediate species, which decomposes at a later stage exothermically (similar to compounds 20 and 33). Various decomposition paths and mechanisms are possible. The tendency of vaporization of the ligands and the relating bond strength of the coordinating tetrazoles is strongly dependant on the metal (MnCl<sub>2</sub> (3) vs.  $CuCl_2$  (4)/ ZnCl<sub>2</sub> (5)), anion  $(Ni(NO_3)_2$  (9) vs  $Ni(ClO_4)_2$  (18)) and the corresponding coordination environment of the complexes. For example, the monodentate picrate complex 32 disintegrates in two stages (loss of two ligands followed by exothermic event) whereas the bidentate styphnate complex 36 decomposes in only one single stage.



Figure 11 TGA measurements (5 ° min<sup>-1</sup>) of the selected compounds.

The thermal stability of the metal(II) MTZ perchlorate complexes (Figure 12) increases in the following order:  $Cu^{2+}$  (211 °C) < Fe<sup>2+</sup> (213 °C) < Zn<sup>2+</sup> (221 °C) < Mn<sup>2+</sup> (223 °C) < Co<sup>2+</sup> (253 °C) < Ni<sup>2+</sup> (271 °C). For previous compounds a similar trend has been reported in literature.<sup>43</sup> The cocrystal perchlorate complexes **21–26** (Figure 13) as well as the chlorides **6/7** lose their cocrystallized MTZ molecules in the range between 66–111 °C and are slightly less temperature stable than their corresponding perchlorate compounds **15–20**. The aqua ligand and crystal water containing complexes can by dehydrated after heating demonstrated by an endothermic peak in the DTA/DSC plots or by weight loss during the TGA measurements.

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Figure 12 DTA plots (5 ° min<sup>-1</sup>) of the perchlorate complexes 15–20.



**Figure 13** DTA plots (5 ° min<sup>-1</sup>) of the perchlorate cocrystal compounds **21–26**.

The sensitivities toward impact, friction and electrostatic discharge for the compounds were determined according to BAM standards. In addition, the compounds have been classified in accordance to the "UN Recommendations on the Transport of Dangerous Goods" using the measured values. An overview of the sensitivities is given in Table 3. The uncoordinated ligand 1 has sensitivities greater than 40 J, greater than 360 N for friction and an ESD value of 1.50 J and can therefore be classified as insensitive. The chloride complexes 3-8 are insensitive toward impact, friction and ESD. Introduction of oxidizing anions like nitrates, cyanodinitromethanides, picrates or styphnates increases the sensitivity against impact, friction and ESD under most circumstances (impact: 2-40 J; friction: 160-360 N; ESD: 0.13-1.50 J). All water-free complexes with trinitrobenzenederivatives as anions are more sensitive toward mechanical stimuli compared with their crystal water or aqua ligand containing analogs. The perchlorate complexes 14-26 are sensitive toward impact (1-10 J) and vary from sensitive to very sensitive against friction (54-216 N). The stability toward impact of the [M<sup>II</sup>(MTZ)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> complexes (Figure S28) decreases in the order:  $Zn^{2+}$  (10 J) <  $Mn^{2+}$  (7 J) <  $Ni^{2+}$  (5 J) <  $Co^{2+}$  $(3 \text{ J}) < \text{Cu}^{2+} (2.5 \text{ J}) < \text{Fe}^{2+} (1 \text{ J})$  and in the following order toward friction:  $Zn^{2+}$  (120 N)  $\approx$  Mn<sup>2+</sup> (120 N) < Ni<sup>2+</sup> (60 N)  $\approx$  Co<sup>2+</sup> (60 N)  $\approx$  Fe<sup>2+</sup> (60 N) < Cu<sup>2+</sup> (54 N). Similar trends have been observed in literature in correlation to energetic metal(II)

diaminotetrazole perchlorate complexes.<sup>44</sup> Cocrystallization of the nitrogen-rich ligand (**21–26**) leads in most cases to a decrease in sensitivities toward mechanical stimuli in comparison to the related perchlorate complexes (Figure S29) while maintaining its highly energetic character and is therefore a great concept for the desensitization of energetic complexes (Figure 14).

Table 3. Ser	Sensitivities toward impact, friction and ESD of 1, 3–10, 12–27 and 29–37.			
	<i>IS</i> (J) <sup>[a]</sup>	<i>FS</i> (N) <sup>[b]</sup>	<i>ESD</i> (J) <sup>[c]</sup>	grain size (μm)
1	> 40	> 360	1.50	< 100
3	> 40	> 360	1.50	100-500
4	> 40	> 360	1.30	500-1000
5	> 40	> 360	1.50	< 100
6	> 40	> 360	1.00	< 100
7	> 40	> 360	0.80	< 100
8	> 40	> 360	1.50	< 100
9	> 40	324	1.50	100-500
10	> 40	> 360	0.40	100-500
12	> 40	> 360	1.50	100–500
13	40	160	0.15	< 100
14	9	160	0.036	< 100
15	7	120	0.08	< 100
16	1	60	0.10	< 100
17	3	60	0.50	< 100
18	5	60	0.10	< 100
19	2.5	54	0.08	< 100
20	10	120	0.25	< 100
21	7	216	0.46	100-500
22	10	120	0.40	100-500
23	10	80	0.13	500-1000
24	6	192	0.20	< 100
25	7	72	0.20	500-1000
26	10	144	0.60	100-500
27	4	324	1.50	100-500
29	> 40	> 360	1.00	100-500
30	> 40	> 360	1.50	100-500
31	4	> 360	0.30	500-1000
32	15	> 360	0.25	100-500
33	15	288	0.20	100-500
34	25	> 360	0.23	100-500
35	25	> 360	0.15	< 100
36	2	160	1.50	100-500
37	4	240	0.80	500-1000

[a] Impact sensitivity according to the BAM drophammer (method 1 of 6); [b] friction sensitivity according to the BAM friction tester (method 1 of 6); [c] electrostatic discharge sensitivity (OZM ESD tester); Impact: insensitive > 40 J, less sensitive  $\geq$  35 J, sensitive  $\geq$  4 J, very sensitive  $\leq$  3 J; Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N and > 80 N, very sensitive  $\leq$  80 N, extremely sensitive  $\leq$  10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.

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Figure 14 Comparison of the impact and friction sensitivities of both the metal perchlorates with and without cocrystallization of 1-methyl-5*H*-tetrazole (1).

Hot needle and hot plate tests of the investigated compounds **16**, **19** and **25** showed deflagrations (Figure 15 and Figure S30– 33). The samples were fixed on an copper plate using adhesive tape. Detonation of the compound typically indicates a valuable primary explosive. The safe and practicable hot plate test shows only the behavior of the unconfined sample toward fast heating on a copper plate. It does not necessarily allow any conclusions on a compound's capability as a primary explosive.



Figure 15 Moment of deflagration of compound 16 during the hot needle tests (left) and hot plate test (right).

#### Toxicity

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The toxicity of the uncoordinated free ligand 1-methyl-5*H*-tetrazole (1) was determined together with the most promising perchlorate complexes **16**, **19** and **25** using the known luminescence bacteria inhibition test in aqueous media.<sup>45</sup> The luminescent marine bacterium Vibrio fischeri NRRL-B-11177, which is part of the commercially available bioassay system LUMIStox, is a representative species for other aquatic organisms and therefore a valuable indicating

device when it comes to groundwater contamination. The half maximal effective concentration EC<sub>50</sub> of these compounds was determined after an incubation time of 30 min.. This toxicological parameter is defined as concentration of the investigated compound, at which the bioluminescence of the bacteria strain is halved after a certain exposure time (e.g 15 or 30 min) and then compared to the original bioluminescence of the sample before being treated. With EC<sub>50</sub> (30 min) values of 5.45 g/L for the free tetrazole 1 and 1.66 g/L for the iron(II) perchlorate complex 16, both compounds can be considered as non-toxic (toxicity level after 30 min incubation: very toxic < 0.10 g/L; toxic 0.10-1.00 g/L; non-toxic > 1.00 g/L).<sup>46</sup> As expected, the copper(II) perchlorate compounds showed half maximum effective concentrations of 0.13 g/L for 19 and 0.26 g/L for 25. Therefore, both complexes have to be classified as toxic, which is not surprising, due to the known toxicity of copper compounds toward microorganisms.<sup>4</sup>

#### Laser initiation

Chavez et al. and our group showed that iron(II) and copper(II) perchlorate complexes of suitable ligands can be initiated in laser ignition experiments.<sup>22,48</sup> These compounds could be potential candidates for laser ignition systems in the future. About 15 mg of the carefully pestled complex to be investigated were filled into a transparent plastic cap, pressed with a pressure force of 1 kN and sealed by a UV-curing adhesive. The laser initiation experiments were carried out with a 45 W InGaAs laser diode operating in the single-pulsed mode. The diode was connected to an optical fiber with a core diameter of 400  $\mu m$  and a cladding diameter of 480  $\mu m.$  The optical fiber was coupled via a SMA type connecter directly to the laser and to a collimator. This collimator was linked to an optical lens, which was positioned in its focal distance (f =29.9 mm) to the sample. The lens was protected from the explosive by a sapphire glass. Only complexes with sensitivities in the range of PETN (IS:  $\geq$  2.5 J, FS:  $\geq$  54 N) were tested in laser initiation experiments. These compounds show slightly increased sensitivities toward mechanical stimuli but are still safe to handle. The confined samples were irradiated at a wavelength of 915 nm, a pulse length of 15 ms, a varying current of 7–10 A and a voltage of 4 V, which combined results in an approximately energy output of 26-60 mJ. The investigated compounds (14-20, 22, 24, 25, 27, 31, 36, 37) showed different responses to the laser irradiation depending on the used metal(II) and anion.

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Figure 16 Moment of deflagration of compound 22 shown as sequence.

The results of these tests are summarized in Table 4. No reaction was observed for the complexes 15, 17, 19 and 37 under the employed laser parameters. The other compounds could be initiated showing decompositions for 27/31, deflagrations for 14, 16, 19, 22, 24, 25 and 36 (Figure 16 and Figure S34–38) and detonation of compound 19 (Figure 17). The complexes exhibit different laser initiation thresholds at comparable sensitivities toward mechanical stimuli. The two cocrystallized MTZ molecules in 25 cause a higher initiation threshold in comparison to 19, which is expressed in a higher required energy input. These results correlate with their observed sensitivities and the conclusion of a higher stability of the cocrystals. Consequently, copper(II) complex 19 represents a promising compound with manageable sensitivities, which can be initiated easily by laser at low initiation energies.



Figure 17 Moment of detonation of complex [Cu(MTZ)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (19).

Table 4	Results of the laser ignition tests.			
	7 A	8 A	9 A	10 A
14	-	_	deflag.	-
15	-	-	-	х
16	dec.	-	-	deflag.
17	-	-	-	x
18	-	-	-	deflag.
19	det.	-	-	det.
20	-	-	-	х
22	-	-	-	deflag.
24	-	-	-	deflag.
25	deflag.	deflag.	-	-
27	-	dec.	-	-
31	-	-	-	dec.
36	-	-	-	deflag.
37	-	-	-	x

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(-: not tested, x: no ignition, dec.: decomposition, deflag.: deflagration, det.: detonation). Operating parameters: current I = 7–10 A; voltage U = 4 V; theoretical maximal output power P<sub>max</sub> = 45 W; theoretical energy E<sub>max</sub> = 26–60 mJ; wavelength  $\lambda$  = 915 nm; pulse length  $\tau$  = 15 ms.

#### UV-Vis spectroscopy

The solid state UV-Vis spectra for the complexes **14–27**, **31** and **36** were collected in the wavelength range of 350–1000 nm in order to get a better understanding of the laser ignition process. Observed optical properties are summarized in Table 5. The step in the absorption intensity at 800 nm in the spectra is caused by a detector change. The UV-Vis spectra exhibit only qualitative character. Selected complexes of different metal centers are exemplarily shown in Figure 18.



Figure 18 UV-Vis spectra in the solid state of selected complexes.

The coordination compounds had absorptions in the UV, visible and near-infrared region typical for the corresponding transition metals. These transitions can be assigned to the characteristic d-d-transitions and correlate with the complementary colors. As expected, the  $d^5$  manganese(II) and  $d^{10}$  zinc(II) complexes showed no absorptions in the measured range and are illustrated together with the cocrystallized perchlorate compounds in the Supporting Information (Figure S39). The cocrystals diverged only minimally from their regular

analogues. In addition, the copper(II) cyanodinitromethanide and trinitrobenzene derivative complexes **27**, **31** and **36** also have strong absorptions ranging from the UV to the visible region of the electromagnetic spectrum (Figure S40). These observations indicated the expected presence of additional electronic transitions in these compounds caused by the coordinating anions ( $n-\pi^*$ : 358 (**27**); 380 (**31**); 404 (**36**) nm).

Table 5	Optical properties of 14-27, 31 and 36.			
	М	color	$\lambda_{d-d}^{[a]}$	$\lambda_{915}/\lambda_{d-d}^{[b]}$
14	Co <sup>Ⅲ</sup> (/s)	orange	463	0.14
15	Mn <sup>II</sup>	colorless	-	-
16	Fe <sup>"</sup> ( <i>hs</i> )	colorless	887	0.99
17	Co"	orange	464, 960	0.64
18	Ni <sup>II</sup>	purple	536, 883	0.75
19	Cu <sup>"</sup>	blue	663	0.46
20	Zn <sup>"</sup>	colorless	-	-
21	Mn <sup>II</sup>	colorless	-	-
22	Fe <sup>"</sup> ( <i>hs</i> )	colorless	883	0.99
23	Co"	orange	467, 961	0.59
24	Ni <sup>II</sup>	purple	547, 904	0.84
25	Cu <sup>II</sup>	blue	676	0.42
26	Zn"	colorless	-	-
27	Cu <sup>"</sup>	blue	358 <sup>[c]</sup> , 612	0.53
31	Cu <sup>"</sup>	green	380 <sup>[c]</sup> , 630	0.74
36	Cu <sup>"</sup>	green	404 <sup>[c]</sup> , 657	0.69

[a] absorption intensity maximum wavelength, which can be assigned to electron d-d excitations in the measured range of 350–1000 nm; [b] quotient of the absorption intensity at the laser wavelength and the intensity at the d-d absorption wavelength; [c]  $n-\pi^*$  transitions.

The laser initiation mechanism is still not fully understood.<sup>49</sup> Many different reaction pathways (e.g. electronically or thermally) are imaginable. Simply regarding the absorption of the complexes at the laser wavelength of 915 nm as shown in Figure 18 and Table 5, one might derive a direct correlation to the performed laser ignition. In contrast to that, the examined Co(II) compound 17, which clearly absorbs in the corresponding region, showed no reaction after exposure to laser irradiation. For MTZ complexes of iron(II) it is well known that the structure in the crystal as well as the counterion (e.g. ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) can have an profound effect on for example the spin crossover properties.<sup>50</sup> It is possible that not only the absorption properties but also subtle changes in the geometry or crystal packing influence the susceptibility of the complexes to laser ignition. The underlying initiation processes are likely to depend on multiple different parameters. Based on the presented results, a general tendency has been observed, that the examined compounds are more likely to deflagrate/detonate by applying laser irradiation if they exhibit high mechanical sensitivities. Due to the fact that the ligands' influence on the laser initiation process, as well as the process itself has not been clarified yet, future investigation will be necessary to fully understand the laser initiation of energetic materials.

The nitrogen-rich heterocycle 1-methyl-5*H*-tetrazole (1, MTZ) was synthesized in a one-step synthesis by methylation of 1,5H-tetrazole. The resulting isomeric mixture was purified by distillation and yielded the desired product in a yield of 48 %. In order to develop new laser-ignitable and environmentally benign primary explosives, diverse energetic coordination compounds were synthesized and characterized. Present energetic transition metal complexes are built up by the nitrogen-rich ligand 1-methyl-5-tetrazole, a transition metal (Mn, Fe, Co, Ni, Cu, Zn and Ag) and oxidizing anions such as perchlorate, nitrate, cyanodinitromethanide, picrate and styphnate. The synthetic route to these complexes is simple, low-cost and fulfills environmental requirements. 31 new coordination compounds, based on MTZ as the monodentate ligand, were prepared and comprehensively characterized. Thermal analysis by DTA showed thermal stabilities with exothermic decomposition temperatures higher or equal to 200 °C for most of the complexes (except 12 and 13). Extraordinary endothermic events such as loss of MTZ and water during the DTA measurements were further investigated by thermal gravimetric analysis. Interesting results in terms of the decomposition pathways of selected compounds were achieved. In addition, X-ray crystal structures were determined for 28 complexes to get better insight into the interesting and challenging complex units showing (except for 13) octahedral coordination spheres. To explore the structural diversity and to tailor the optical and energetic properties of these complexes, seven different metals and seven different ligands/counteranions (Cl, NH<sub>3</sub>, NO<sub>3</sub>, ClO<sub>4</sub>, CDNM, PA, HTNR) were used. Preparation of the metal perchlorate complexes 15-20 was strongly dependent on the stoichiometry of the ligand and vielded complex units without and with (21-26) two cocrystallized tetrazoles. Cocrystallization of the endothermic MTZ molecule leads in most cases to a decrease in sensitivities toward mechanical stimuli while maintaining its highly energetic character and is therefore an excellent concept for the desensitization of energetic coordination compounds. Environmentally benign iron and copper complexes 16, 19 and 25 were also evaluated for use as primary explosives by hot needle tests, hot plate tests and toxicity assessments. Laser ignition experiments, which were carried out at a wavelength of 915 nm and a pulse length of 15 ms showed detonation of compound 16 (IS: 2.5 J, FS: 54 N,  $T_{exo}$ : 211 °C). The successful initiation makes 16 to a promising candidate for future laser initiation systems.

#### **Conflicts of interest**

"There are no conflicts to declare".

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An extensive study on 31 new energetic coordination complexes was carried out using 1-methyl-5*H*-tetrazole as the nitrogen-rich ligand. Energetic coordination compounds show potential use in mechanical or optical initiation systems. Their energetic character can be adjusted by using different metal centers (Mn<sup>II</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Ag<sup>I</sup>) and counter anions (e.g. NO<sub>3</sub>, ClO<sub>4</sub>, picrate, styphnate). A consistent series of cocrystallized complexes was achieved by using an excess of the ligand and compared to the classical complexes.