



## Highly Functional Energetic Complexes: Stability Tuning Through Coordination Diversity of Isomeric Propyl-linked Ditetrazoles

Journal:	<i>Journal of Materials Chemistry A</i>
Manuscript ID	TA-ART-02-2018-001412.R1
Article Type:	Paper
Date Submitted by the Author:	07-Mar-2018
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Journal Name

ARTICLE

## Highly functional energetic complexes: stability tuning through coordination diversity of isomeric propyl-linked ditetrazoles

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Currently used primary explosives suffer from various drawbacks like insidious sensitivities toward mechanical stimuli and electrostatic discharge, but also from environmental concerns largely attributed to toxic lead compounds. These issues can directly be related to higher risk during processing and handling of these sensitive materials. In this research, 12 new lead-free energetic coordination compounds (ECC) based on three isomeric propyl-linked ditetrazoles as ligands with moderate sensitivities are described, which can be initiated reliable and safely by irradiation with near infrared light (NIR). Excellent thermal stabilities for all complexes up to an outstanding decomposition temperature of 297 °C for compound **7** could be achieved through the formation of stable polymeric networks. The optical and energetic properties of these complexes can easily be customized by variation of various building blocks like different transition metals (Mn<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Ag<sup>+</sup>), anions (perchlorate, styphnate, cyanodinitromethanide and dinitramide) and for the first time by the use of three different isomeric ditetrazole ligands. 1,3-di(tetrazol-1-yl)propane (1,1-dtp), 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (1,2-dtp) and 1,3-di(tetrazol-2-yl)propane (2,2-dtp) were prepared in a convenient and straightforward one-step alkylation reaction of 1,5H-tetrazole. The obtained compounds were extensively characterized by e.g. XRD, IR, EA, UV/Vis and DTA. In addition, the sensitivities toward external stimuli (impact, friction and electrostatic discharge) were determined according to *Bundesamt für Materialforschung und -prüfung (BAM)* standard methods. The iron(II) **5** and copper(II) perchlorate complexes **8**, **11** and **12** show promising characteristics and could be potential candidates for possible applications in the future.

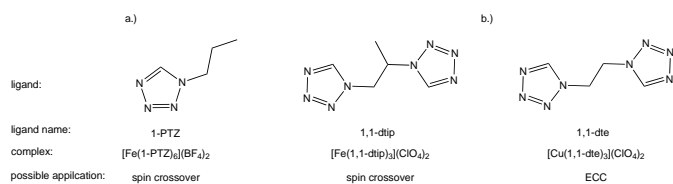
### Introduction

The first tetrazole compound mentioned in the literature, 1-phenyl-1H-tetrazole-5-carbonitrile, was accidentally synthesized by the Swedish chemist J. A. Bladin in 1885 at the University of Uppsala.<sup>1</sup> Since then numerous compounds based on this five-membered heterocycle have been prepared and extensively characterized.<sup>2–4</sup> Particularly in the challenging field of coordination chemistry, tetrazole ligands have proven to be versatile components that form a large number of functional materials.<sup>5,6</sup> These compounds show promise in many different applications ranging from molecular magnetism in spin-crossover systems,<sup>7,8</sup> porous metal-organic frameworks (MOFs) for potential gas storage,<sup>9</sup> and possible use as energetic materials such as secondary and primary explosives.<sup>10,11</sup>

The spin crossover (SCO) phenomenon, wherein the spin state of the compound alters in consequence of an external stimuli (specific temperature, pressure or light irradiation), has attracted considerable attention in recent years.<sup>12</sup> Especially iron(II) complexes, but also other transition metals with d<sup>4</sup> to d<sup>7</sup> electronic configuration coordinated by alkylated mono- and ditetrazoles (Chart 1a) in combination with various counter-anions like ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup>, showed this behavior. The phenomenon appears as a result of the interaction between the electron-electron repulsion and the dependence of the ligand-field strength on the metal to ligand distance.<sup>13</sup> The complexes showed two different lattice sites for the metal centers with a spin transition (*hs* to *ls*) depending on the applied temperature. Emission of electromagnetic waves with wavelengths in the green or red region can initiate metastable long-lived *hs* and *ls* states on both sides, which makes these compounds attractive for use as molecular switches or in liquid crystals.<sup>14</sup> In contrast to magnetic properties, very little is known of transition metal complexes in association with energetic materials (Chart 1b), although these compounds could indeed solve two basic problems of current primary explosives: high toxicity and high sensitivity. Toxic compounds like lead azide and lead styphnate are still the main

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Electronic Supplementary Information (ESI) available: IR spectroscopy of **1–15**; X-ray Diffraction; DTA plots of **1–3**, **8** and **10–15**; Column diagrams of the complexes **8** and **11–15**; Hot plate and hot needle tests; Laser ignition tests; UV-Vis spectra of **4**, **9**, **10** and **13–15**; Experimental part and general methods. See DOI: 10.1039/x0xx00000x

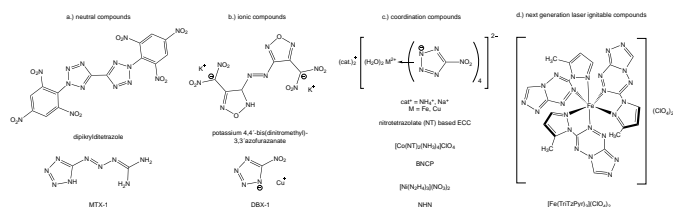
components in most priming compositions today. Due to the potential risk to the human health and the environment, many scientists from around the world are searching for alternatives with partly different approaches.<sup>15–18</sup>



**Chart 1** Overview of selected mono- and ditetrazole ligands in combination with different metal salts proposed as: (a) spin crossover compounds or (b) ECC.<sup>19–21</sup>

Possible solutions comprise the use of non-toxic and sensitive: (a) neutral,<sup>22,23</sup> (b) ionic<sup>24,25</sup> or (c) coordination compounds (Chart 2).<sup>26–28</sup> Energetic coordination compounds (ECC) fulfill most of the desired requirements (low-cost, high yields, good compatibilities, low environmental impact, low toxicities etc.) and are therefore promising candidates for future applications in the field of high energy dense materials.<sup>29–31</sup>

Energetic complexes hold great potential in the area of optical initiation, which offers various benefits over conventional systems (electrical, mechanical, thermal).<sup>32</sup> The risk of accidental initiation by unintended impulses (impact, friction, ESD) can be minimized through application of less sensitive explosives (Chart 2d) with the consequence of an easier processing and handling of these materials.<sup>33</sup> A further advantage of laser ignition is a shorter response time toward initiation pulses after irradiation by NIR, which allows safer and more reliable initiation of the materials.<sup>34</sup>

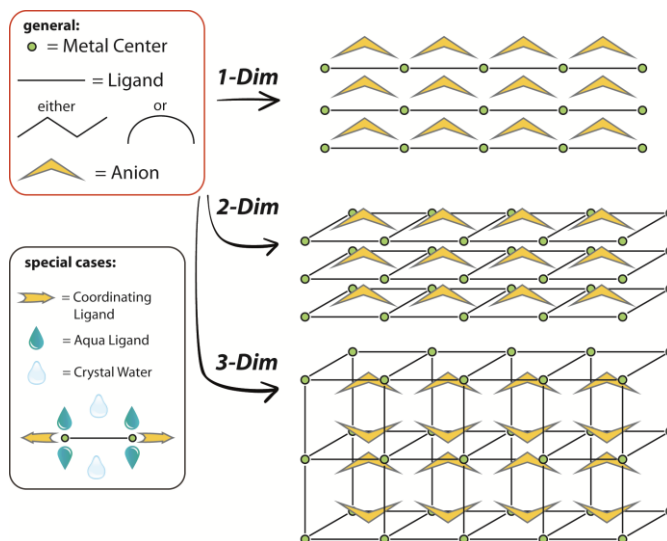


**Chart 2** Different synthetic approaches in order to replace lead containing primary explosives through: (a) neutral,<sup>22,23</sup> (b) ionic<sup>24,25</sup> or (c) coordination compounds,<sup>26–28</sup> (d) new generation of laser ignitable explosives.<sup>33</sup>

Many recently developed primary explosives are struggling to meet the desired criteria regarding thermostability, which are particularly important for special applications in industry (e.g. mining and oil drilling).<sup>35</sup> Especially complex monomers without extended structures suffer from low thermal stabilities, which can most likely be attributed to a high vapor pressure of the ligands in combination with relatively weak coordination bonds.<sup>6</sup>

In order to overcome the lack in thermal stability, modifications and further developments were made and bidentate bridging tetrazole ligands implemented into the ECC to build up stable multidimensional (1D, 2D or 3D) polymeric networks (MOFs, Figure 1). In the past, investigations of the physico-chemical properties of these tetrazole based energetic complexes as well as toxicological studies toward aquatic life have proven the great suitability of these ligands.<sup>6,17</sup> For this

purpose, three different isomeric propyl linked ditetrazoles prepared in a convenient one step reaction were selected, which until now, have only been described in correlation with magnetic studies in spin transition experiments.<sup>36,37</sup> Desired physicochemical properties of the compounds were easily adjusted by variation of the metal, the anion and for the first time by application of different isomers with varying complexation patterns resulting in a great coordination diversity. In this contribution, reasonable efforts have been made to use these nitrogen-rich ligands as building blocks for the preparation of new energetic coordination polymers with desired characteristics, such as thermally stability and laser-ignitibility.



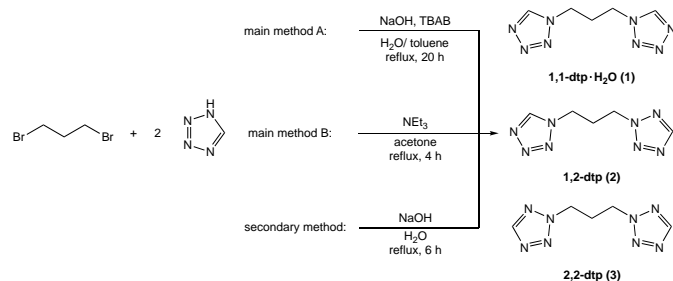
**Figure 1** Concept of thermostability in energetic coordination compounds (ECC) achieved through the assembly of multidimensional (1D, 2D or 3D) polymeric networks (MOFs) based on bidentate bridging ditetrazole ligands.

## RESULTS AND DISCUSSION

### Synthesis

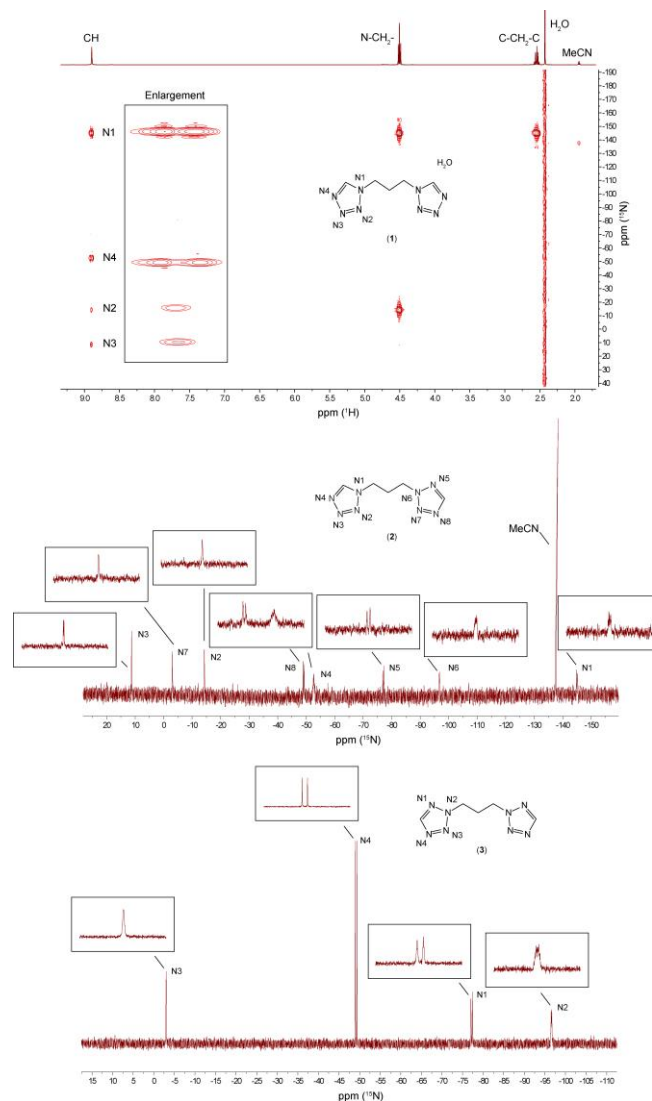
Various synthetic pathways toward tetrazole derivatives have been reported in the literature providing an easy access to this class of compounds.<sup>38</sup> One commonly used route starts from primary amine precursors and enables the preparation of N1-substituted tetrazoles free of other regioisomers.<sup>39,40</sup> Corresponding amines cyclize after treatment with sodium azide and triethyl orthoformate under acidic conditions in a [2+3] cycloaddition reaction. However, the synthesis of 1,3-di(tetrazol-1-yl)propane (1,1-dtp) via this conventional route fails and isolation of the desired compound is not possible. Therefore, two synthetic protocols have been developed, including the nucleophilic substitution reaction of 1,3-dibromopropane by sodium 5H-tetrazolate under various conditions.<sup>36,37</sup> However; this alkylation method affords an isomeric mixture containing not only 1,1-dtp but also the N2-substituted 1,3-di(tetrazol-2-yl)propane (**3**, 2,2-dtp) and the mixed N1,N2-substituted 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (**2**, 1,2-dtp). Both heterocycles, which have already been described in the literature, cannot be synthesized directly

as regioisomerically pure and suffer from the same issues as 1,1-dtp.<sup>41–43</sup> Therefore, an extensive investigation was carried out on the synthesis, purification and isolation of all three isomers from one reaction mixture by different preparative strategies (Scheme 1). After evaluation and comparison of these methods, information regarding the influence of a phase transfer catalyst, varying solvents, organic/inorganic bases and a differing work-up on the reaction products (yield and ratio) were obtained and are summarized in Table 1. All syntheses examined used 1,5H-tetrazole as the starting material, which was deprotonated to the corresponding tetrazolate salt by sodium hydroxide (main method A and secondary method) or by triethylamine (main method B) and further reacted with the alkylating agent 1,3-dibromopropane in a nucleophilic substitution reaction. In contrast to other described syntheses using solely acetone or water as solvents, method A included the use of a phase transfer catalyst (TBAB = tetrabutylammonium bromide) in combination with a water/toluene solvent mixture to facilitate the dispersion of the reactants. Heating of the reaction mixtures to reflux for a certain time period was accompanied with the formation of the associated bromide salts (sodium bromide or triethylammonium bromide), which were separated later during the work-up process. Separation of the crude material was accomplished through flash column chromatography on silica gel partly and through extraction and addition of different organic solvents (main method B and secondary method) based on the different polarities of the three isomers. Further details on the work-up procedures can be found in the experimental section.



**Scheme 1.** Preparation of the propyl-linked ditetrazole isomers **1–3** via different synthetic pathways.

The highest overall yield was observed for method A with a value of 71%, followed by 66% for method B and only 17% for the secondary method. A possible explanation for the low yield of the secondary method could be an incomplete reaction of the starting materials due to the bad solubility of the reactants in water and losses during the work-up. Selectivity of alkylation is mainly dominated by the electronic structure of the substituents at the heterocycle and favors the formation of the mixed N1,N2-substituted ditetrazole **2**. Distinction of the obtained isomers can easily be made by infrared spectroscopy (Figure S1), <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. In addition, proton coupled <sup>15</sup>N NMR or two dimensional <sup>1</sup>H, <sup>15</sup>N NMR HMBC spectroscopy can be applied (Figure 2).



**Figure 2** Two dimensional <sup>1</sup>H, <sup>15</sup>N HMBC NMR spectrum of **1** and proton coupled <sup>15</sup>N NMR spectra of **2** and **3**.

Various coordination compounds based on 1,2-di(tetrazol-5-yl)ethane (1,1-dte) as the ligand have shown promising results during laser initiation experiments in the past but were too sensitive for any application.<sup>17</sup> In order to increase the stability, ditetrazolypropane ligands with higher carbon contents were used for the synthesis of new complexes in this contribution. The main focus was put on the analogous N1,N1-substituted ditetrazole (1,1-dtp), which has been proven to be an extraordinary ligand for the preparation of new energetic materials. Our synthetic concept includes the formation of neutral coordination compounds or complex cations with integrated oxidizing anions like perchlorates, trinitrorescorcinates (TNR), cyanodinitromethanides or dinitramides enabled through the incorporation of neutral non-acidic ligands. Copper(II) perchlorate containing energetic coordination compounds have shown to be very promising in laser initiation experiments and were synthesized in combination with three different propyl-linked ditetrazoles.<sup>44</sup>

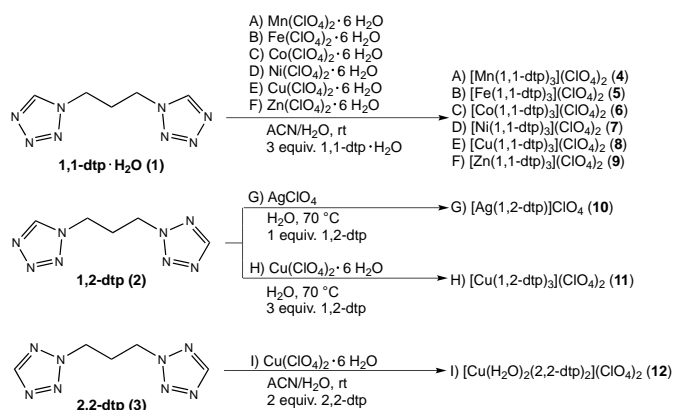
**Table 1.** Overview of the different methods, associated yields and isomer ratios.

	main method A	main method B	secondary method
<b>base</b>	NaOH	NEt <sub>3</sub>	NaOH
<b>solvent</b>	water/toluene	acetone	water
<b>temp./ time</b>	reflux/ 20 h	reflux/4 h	reflux/6 h
<b>phase transfer cat.</b>	TBAB	—	—
<b>work-up</b>	column chromatography	desorption/ column chromatography	extraction/ column chromatography
<b>1,1-dtp • H<sub>2</sub>O</b>	12%	9%	8%
<b>1,2-dtp</b>	41%	33%	6%
<b>2,2-dtp</b>	18%	24%	3%
<b>overall yield</b>	71%	66%	17%

Synthesis of the coordination compounds **4–12** was achieved via combination of the associated metal(I,II) perchlorate salts and the respective ditetrazole ligands **1–3** in the corresponding stoichiometries at room temperature (Scheme 2). Exclusive use of water as solvent in the synthesis of **4–9** lead to the precipitation of compound **1** among the desired complexes due to the low solubility of **1** in water. In order to increase the solubility of the organic alkylated heterocycles, a mixture of water and acetonitrile was chosen as solvent and only small quantities were used to ensure fast crystallization of the desired complexes.

Coordination compounds **5** and **7** have already been described in relation to the SCO phenomenon and were prepared to close their physico-chemical gaps.<sup>37</sup> In addition, an intensive investigation and characterization of their energetic character has been conducted. All compounds (except **7**) were analyzed by single crystal diffraction. The nickel(II) perchlorate complex **7** precipitated, in contrast to the isotopic 1,1-dtp coordination compounds, as an amorphous powder and all recrystallization attempts failed to achieve single crystals. After comparison of the infrared spectra of **4–9** and elemental analysis, a complex composition of [Ni(1,1-dtp)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> can be presumed for coordination compound **7**, analogous to the other perchlorate complexes (Figure S2).

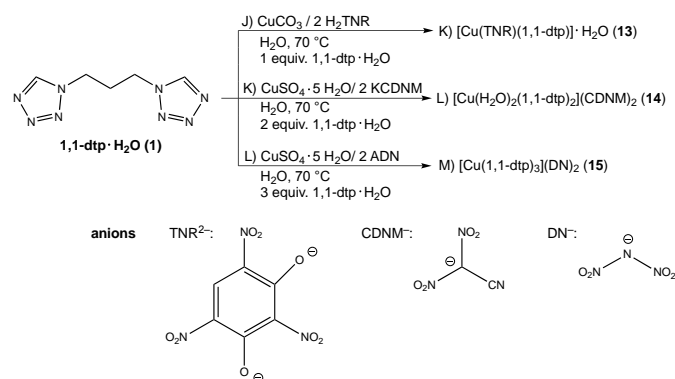
The nitrogen-rich compound 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (**2**), which has been successfully inserted into the silver(I) and copper(II) perchlorate complexes (**10** and **11**), was used for the first time as ligand in transition metal complexes. Each complex exhibits different absorptions in the infrared spectra showing a bidentate (**11**) or a tetradentate (**10**) complexation of the metal centers (Figure S3). The attempted preparation of silver(I) complexes with ligand **1** and **3** was unsuccessful.

**Scheme 2.** Synthesis of the metal(I,II) perchlorate complexes **4–12** based on different propyl-linked ditetrazole ligands.

The majority of the complexes could be achieved without crystal water or aqua ligand inclusion. This has a significant influence on the stability and performance of the compounds leading to more powerful molecules. Complex **12** crystallizes, in contrast to the reported copper(II) perchlorate coordination compound, as a diaqua species, which contains only two dtp ligands independent of the stoichiometry applied (2 equiv. vs. 3 equiv.).<sup>42</sup>Fehler! Textmarke nicht definiert. A possible explanation could be the formation of a kinetic ([Cu(2,2-dtp)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>) complex first, which reacts slowly with the solvent molecules to the thermodynamic product ([Cu(H<sub>2</sub>O)<sub>2</sub>(2,2-dtp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>). The copper(II) perchlorate complexes described here can easily be distinguished through IR spectroscopy due to the varying complexation manner of the three ditetrazole ligands (Figure S4). In particular, 2,2-dtp containing complexes have shown to crystallize primarily with solvent molecules, lowering the performance of the desired energetic material and making them unsuitable for any application.<sup>42,43</sup>

The commercially unavailable metal(II) salt precursors for the preparation of the coordination compounds **13–15** were synthesized in situ through metathesis or straightforward acid-base reaction between copper(II) carbonate and styphnic acid (H<sub>2</sub>TNR) at 70 °C in water. The corresponding precursors were then reacted with the ditetrazole ligand **1** (Scheme 3) and the lower solubility of the complexes was used as the driving force. Coordination compound **13** precipitated unintentionally as double deprotonated styphnate and crystal water containing complex immediately after addition of the ligand. Due to the low performance of the complex, no other trinitrobenzene containing anion (e.g. picrate) has been employed in the other complexes.

All described coordination compounds were left undisturbed for crystallization and were isolated by filtration after solid material appeared from the mother liquor in form of single crystals within hours or days (except nickel(II) complex **7**). The products were received in reasonable yields (35–89%) after washing with ice-cold ethanol to remove unreacted materials when necessary and drying in air over night.

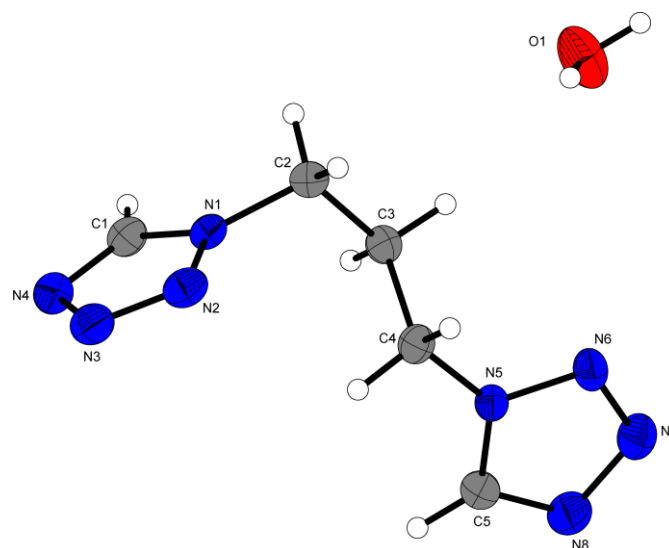


**Scheme 3.** Formation of the copper(II) coordination compounds **13–15** with varying anions ( $\text{TNR}^{2-}$  = trinitrosorcinato,  $\text{CDNM}^-$  = cyanodinitromethanide, and  $\text{DN}^-$  = dinitramide; IR spectra illustrated in Figure S5).

### Crystal structures

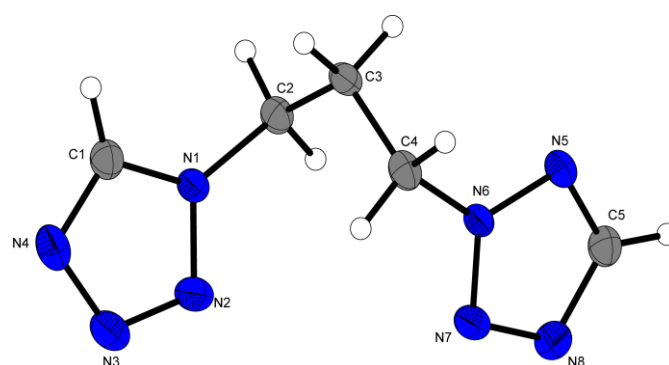
The structure of all compounds including ligands and complexes (except **7**) was determined by low temperature X-ray diffraction. In contrast to the literature, ditetrazole **3** could be solidified through controlled freezing with liquid nitrogen and subsequent thawing to room temperature. The ligand stayed crystalline and single crystal blocks suitable for X-ray diffraction could be measured. Compound **7** emerged in form of an amorphous powder making single crystal experiments impossible. All central atoms, except the silver(I) metal ion in complex **10**, show an octahedral coordination sphere where the complexation to the metal ion takes place by the N4 and N8 nitrogen atoms of the ditetrazolypropanes. Chelation of the ligand is prevented through the rigidity of the propyl chains, which disables the generation of complex monomers and leads to the formation of polymeric structures with varying dimensions by bridging between the metal centres. Poor quality single crystals of complex **13** were measured to get an indication of the most likely appearance of the structure. An appropriate finalization of the data set was not possible due to the strongly disordered moieties and the related weak diffractions. Nonetheless, elemental analysis in combination with infrared spectroscopy (Figure S5) validated its temporary observed structure. Details of the crystal structures of complexes **4**, **5**, **6**, **9**, and **13** are given in the SI together with the measurement and refinement data of all compounds. The crystal structures were deposited in the CSD database<sup>45</sup> and can be obtained free of charge with the CCDC nos. 1816637 (**1**), 1816632 (**2**), 1816943 (**3**), 1816628 (**4**), 1816635 (**5**), 1816627 (**6**), 1816626 (**8**), 1816629 (**9**), 1816630 (**10**), 1816636 (**11**), 1816633 (**12**), 1816631 (**14**), 1816634 (**15**). Compound **1** crystallizes as a monohydrate in the form of colorless blocks in the orthorhombic space group  $Pbca$  with eight formula units per unit cell and a calculated density of  $1.439 \text{ g cm}^{-3}$  at 173 K. One of the tetrazole rings stands in *gauche* (C1, N1–N4) orientation while the other stands in *anti* (C5, N5–N8) conformation to the propyl function (Figure 3), similar to the situation found in the anhydrous compound reported in literature.<sup>36</sup> The bond lengths of the propyl chain (C2–C3  $1.5189(19) \text{ \AA}$  and C3–C4  $1.5184(17) \text{ \AA}$ ) are in the typical range of C–C single bonds and the distances in the tetrazole

rings (N1–C1  $1.3293(16) \text{ \AA}$ , N1–C2  $1.4620(15) \text{ \AA}$ , N4–C1  $1.3092(16) \text{ \AA}$ , N1–N2  $1.3505(14) \text{ \AA}$ , N2–N3  $1.2901(16) \text{ \AA}$  and N3–N4  $1.3673(15) \text{ \AA}$ ) are comparable to that of other 1-substituted tetrazoles.<sup>46</sup>



**Figure 3** Molecular unit of 1,1-dtp ·  $\text{H}_2\text{O}$  (**1**). Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50% probability level. Selected bond angles (°): C2–C3–C4  $112.12(11)$ , N1–C2–C3  $111.38(11)$ , and N5–C4–C3  $110.96(10)$ .

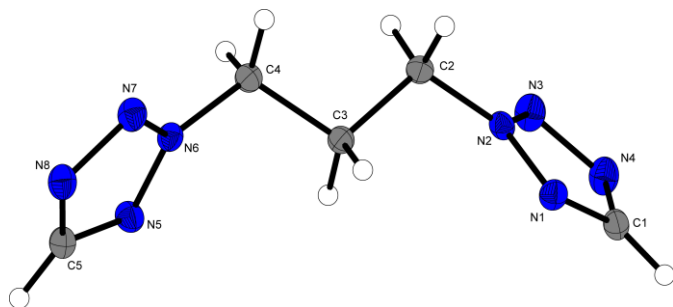
The nitrogen-rich ligand **2** crystallizes in the form of colorless blocks in the monoclinic space group  $P2_1/n$  with four formula units per unit cell and a calculated density of  $1.462 \text{ g cm}^{-3}$  at 173 K. Ligand **2** shows, in contrast to compound **1**, a *gauche* conformation of both tetrazole rings to the propyl group with analogous bond lengths in the ring (C1, N1–N4) and the propyl bridge (Figure 4). In comparison to the other tetrazole moiety, only minor deviations can be observed in the bond lengths for the N2-substituted heterocycle (N5–C5  $1.3249(15) \text{ \AA}$ , N6–C4  $1.4655(14) \text{ \AA}$ , N8–C5  $1.3376(15) \text{ \AA}$ , N5–N6  $1.3265(13) \text{ \AA}$ , N6–N7  $1.3177(12) \text{ \AA}$  and N7–N8  $1.3239(13) \text{ \AA}$ ).



**Figure 4** Molecular unit of 1,2-dtp (**2**). Selected bond lengths(Å): C2–C3  $1.5204(17)$ , C3–C4  $1.5181(16)$ , N1–C1  $1.3308(14)$ , N1–C2  $1.4670(14)$ , N4–C1  $1.3070(16)$ , N1–N2  $1.3453(13)$ , N2–N3  $1.2932(14)$ , N3–N4  $1.3620(15)$ ; selected bond angles (°): C2–C3–C4  $114.57(9)$ , N1–C2–C3  $112.19(9)$ , and N6–C4–C3  $111.93(9)$ .

The N2,N2-substituted ditetrazole ligand **3** crystallizes in the form of colorless blocks in the monoclinic space group  $P2_1/c$  with four formula units per unit cell and a calculated density of  $1.474 \text{ g cm}^{-3}$  at 143 K. The ligand shows unlike compound **1**

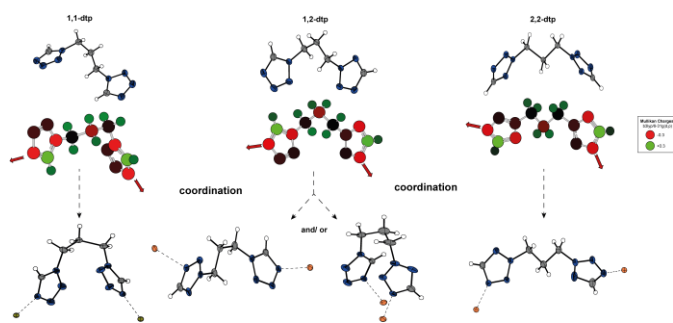
and 1,2-dtp an *anti* conformation of both tetrazole heterocycles to the alkyl bridge but with similar bond lengths in the ring and chain (Figure 5).



**Figure 5** Molecular unit of 2,2-dtp (**3**). Selected bond lengths(Å): C2–C3 1.5209(15), C3–C4 1.5164(15), N1–C1 1.3260(16), N2–C2 1.4593(14), N6–C4 1.4590(15), N1–N2 1.3252(14), N2–N3 1.3200(14), N3–N4 1.3237(14); selected bond angles (°): C2–C3–C4 107.96(8), N2–C2–C3 112.05(8), and N6–C4–C3 112.19(8).

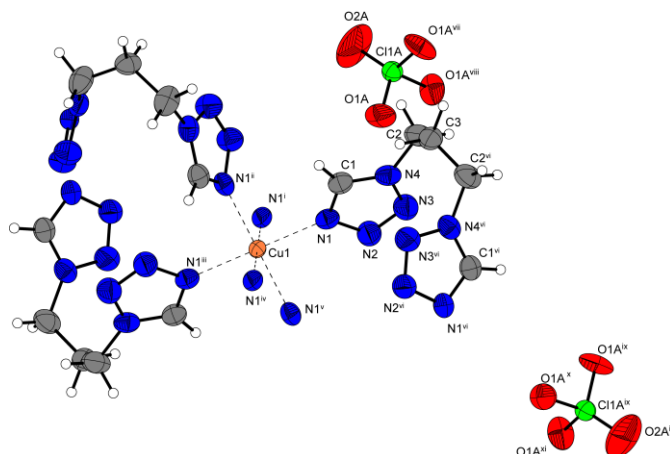
Coordination of the ditetrazole causes a reorientation of the ligands and is shown in Figure 6. The bond lengths of the coordinating ligands in the investigated ditetrazole complexes are in the same range as the uncoordinated ditetrazole compounds **1–3** and are not discussed in detail in any of the following ECC.

The octahedrally coordinated metal(II) perchlorate complexes of heterocycle **1** (**4–6**, **8** and **9**) crystallize all isotypically in the trigonal space group  $P\bar{3}c1$  with two formula units per unit cell showing almost the same metric with varying densities between 1.656 (**4**) and 1.754 g cm<sup>-3</sup> (**5**) (Mn: 1.656 (173 K); Fe: 1.754 (123 K); Co: 1.712 (173 K); Cu: 1.721 (123 K) and Zn: 1.747 (123 K) g cm<sup>-3</sup>). Interestingly the expected Jahn-Teller distortion, typical for d<sup>9</sup> electron configuration, cannot be observed in the structure of copper(II) complex **8** (Figure 7).



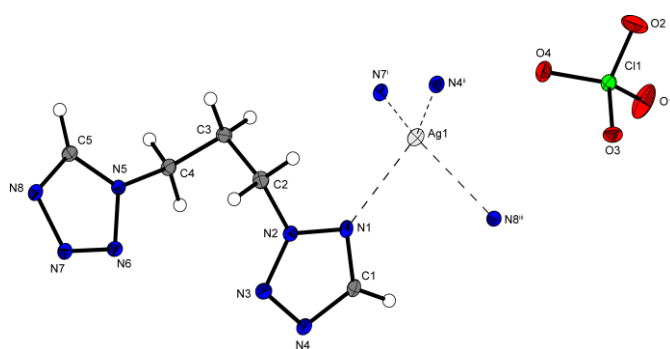
**Figure 6** Reorientation of the ditetrazoles after complexation (except complex **10**) together with the calculated (B3LYP / 6-31G(d,p)) Mulliken charges of the uncoordinated dtp ligands.

Compared to the free ligand, both tetrazole rings are in *gauche* conformation to the propyl chain enabling the formation of polymeric chains made of transition metals(II), where the central atoms are connected by bridging ditetrazole units (Figure S6–9). In all perchlorate 1,1-dtp structures the central methylene units of the propylene bridges and also the perchlorate anions are heavily disordered and had to be refined as split positions.



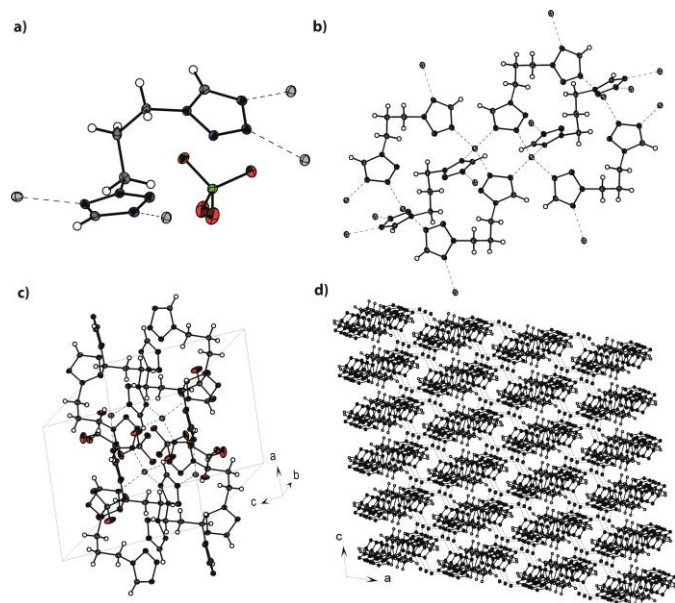
**Figure 7** Copper(II) coordination environment of [Cu(1,1-dtp)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (**8**). Selected bond length (Å): Cu–N1 2.131(2); selected bond angles (°): N1–Cu1–N1<sup>i</sup> 89.33(9), N1–Cu1–N1<sup>iii</sup> 180.00, and N1–Cu1–N1<sup>iv</sup> 90.68(9). Symmetry codes: (i) y, -x+y, 1-z; (ii) x-y, x, 1-z; (iii) -x, -y, 1-z; (iv) -y, x-y, z; (v) -x+y, -x, z; (vi) -x, -x+y, 1.5-z; (vii) -x+y, 1-x, z; (viii) 1-y, 1+x-y, z; (ix) 1+x-y, 1-y, 1.5-z; (x) y, x, 1.5-z; (xi) 1-x, -x+y, 1.5-z.

The d<sup>10</sup> metal(I) perchlorate **10** is the only complex, that shows a tetrahedral coordination sphere. The compound crystallizes in the form of colorless blocks in the monoclinic space group  $P2_1/c$  with four formula units per unit cell and a calculated density of 2.267 g cm<sup>-3</sup> at 123 K, the highest density observed of all compounds. The silver(I) cation is bonded to only one neutral tetradentately (N1, N4, N7, N8) coordinating ditetrazole (Figure 8).



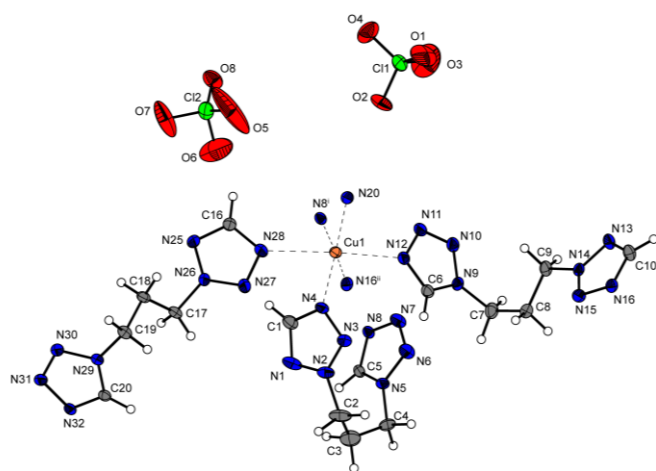
**Figure 8** Silver(I) coordination environment of [Ag(1,2-dtp)]ClO<sub>4</sub> (**10**). Selected bond lengths (Å): Ag1–N1 2.435(2), Ag1–N4<sup>ii</sup> 2.264(2), Ag1–N7<sup>i</sup> 2.265(2), Ag1–N8<sup>iii</sup> 2.365(2); selected bond angles (°): N1–Ag1–N7<sup>i</sup> 105.96(6), N1–Ag1–N8<sup>iii</sup> 83.91(6), N1–Ag1–N4<sup>ii</sup> 109.10(6). Symmetry codes: (i) -x, 0.5+y, 0.5-z; (ii) x, 1.5-y, -0.5+z; (iii) -1+x, 1.5-y, -0.5+z.

The N1-substituted tetrazole bridges through its N3 and N4 donor atoms, whereas the 2-substituted ring binds with the N1 and N4 atoms. Compared to the free uncoordinated ligand, both rings maintain their *gauche* conformation to the propyl chain and each ditetrazolopropane bridges between four different silver(I) atoms (Figure 9 a) and b)) building up a three-dimensional polymeric network with incorporated non-coordinating perchlorate anions (Figure 9c) and d)).



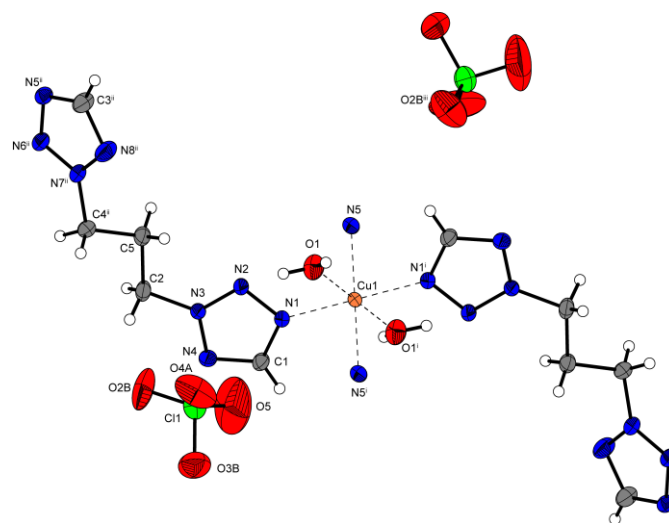
**Figure 9** Coordination in  $[\text{Ag}(1,2\text{-dtp})]\text{ClO}_4$  (**10**): a) Formula unit with the linkage of the ligand between the metal(I) cations; b) bridging pattern of the tetradentately coordinating tetrazole **2** (omission of the perchlorate anions for better clarity); c) unit cell with 4 formula units; d) metal-organic framework (MOFs) depicted along the *b* axis (without perchlorate anions).

Complex **11** with  $1.693 \text{ g cm}^{-3}$  at 123 K shows the lowest density of all copper(II) complexes. It crystallizes in the form of blue rods in the triclinic space group  $P\bar{1}$  with two formula units per unit cell and shows every type of conformation (*gauche/gauche*; *gauche/anti*; and *anti/anti*), in comparison to the free ligand **2**. The complex has an octahedral coordination sphere with six coordinating tetrazoles building up a three-dimensional polymeric network and shows, in contrast to **8**, the expected Jahn-Teller distortion along the axial direction (Figure 10). The inconsistent conformations of the ligand are accompanied by a loss of density.



**Figure 10** Coordination environment of  $[\text{Cu}(1,2\text{-dtp})_3](\text{ClO}_4)_2$  (**11**). Selected bond lengths (Å): Cu1–N4 2.043(4), Cu1–N8 2.020(4), Cu1–N12 2.316(4), Cu1–N16 2.011(3), Cu1–N20 2.031(4), Cu1–N28 2.483(5); selected bond angles (°): N4–Cu1–N12 90.9(2), N4–Cu1–N8 94.1(2), N4–Cu1–N16 87.7(2). Symmetry codes: (i)  $1-x, -y, 1-z$ ; (ii)  $2-x, -y, 1-z$ .

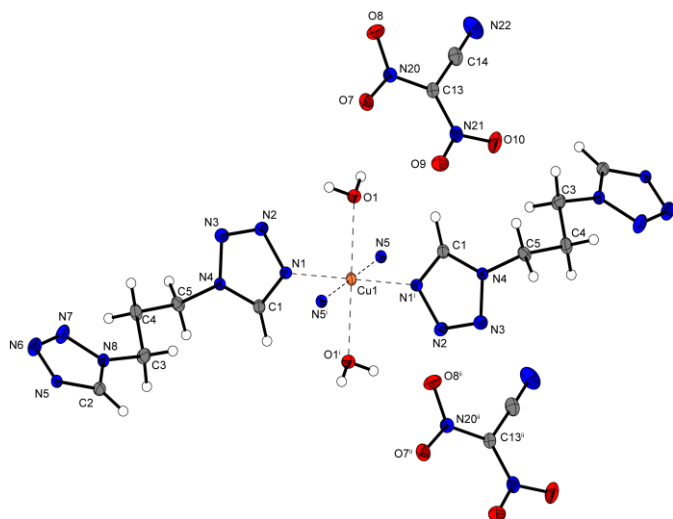
The diaqua complex **12** illustrated in Figure 11 crystallizes in the form of blue blocks in the monoclinic space group  $P2_1/c$  with two formula units per unit cell and a calculated density of  $1.765 \text{ g cm}^{-3}$  at 233 K. Substitution of one ditetrazole through two aqua ligands leads to a slightly higher density in comparison to compound **8** ( $\rho = 1.721 \text{ g cm}^{-3}$ ) and **11** ( $\rho = 1.693 \text{ g cm}^{-3}$ ). Every tetrazole ring of the 2,2-dtp ligand is similar to the uncoordinated compound in *anti* conformation to the propyl chain linking the copper(II) metal center to four other metal ions. The oxygen atoms in axial positions prevent the formation of a 3D-polymeric structure leading to two dimensional layers with two non-coordinating perchlorate counter-anions.



**Figure 11** Copper(II) coordination environment of  $[\text{Cu}(\text{H}_2\text{O})_2(2,2\text{-dtp})_2](\text{ClO}_4)_2$  (**12**). Selected bond lengths (Å): Cu1–O1 2.294(2), Cu1–N1 2.0214(19), Cu1–N5 2.0317(19); selected bond angles (°): O1–Cu1–N1 90.00(8), O1–Cu1–N5 92.60(9), and N1–Cu1–N5 89.52(8). Symmetry codes: (i)  $1-x, -y, 1-z$ ; (ii)  $2-x, 0.5+y, 1.5-z$ ; (iii)  $1-x, -0.5+y, 1.5-z$ .

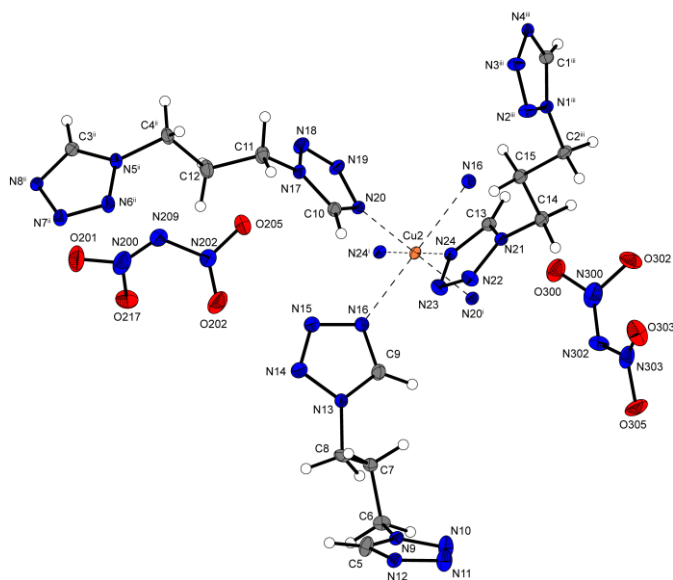
The molecular unit of compound **14** consists of two non-coordinating cyanodinitromethanide counterions and one copper(II) cation, which is coordinated by two axial aqua ligands and four tetrazoles in a plane corresponding to two 1,1-dtps (Figure 12). Compared to the perchlorate complexes of 1,1-dtp, the ligands maintain the conformation with one tetrazole ring in *gauche* and one in *anti* position to the propyl chain preventing the bonding of two additional nitrogen atoms to the metal center. As already observed for compound **12**, the replacement of one ditetrazole through two aqua ligands in **14** leads to a small increase in density ( $1.761 \text{ g cm}^{-3}$ ). The one-dimensional polymeric complex crystallizes in the form of blue blocks in the triclinic space group  $P\bar{1}$  with two formula units per unit cell.





**Figure 12** Copper(II) coordination environment of  $[\text{Cu}(\text{H}_2\text{O})_2(1,1\text{-dtp})_2](\text{CDNM})_2$  (**14**). Selected bond lengths (Å): Cu1–O1 2.3298(15), Cu1–N1 2.0107(15), Cu1–N5 2.0241(15); selected bond angles (°): O1–Cu1–N1 94.98(6), O1–Cu1–N5 89.50(6), and N1–Cu1–N5 90.18(6). Symmetry codes: (i) 1–x, 1–y, 1–z; (ii) –1+x, y, z.

Similar to complex **8**, the octahedral coordination sphere of anhydrous compound **15** consists of six tetrazole rings with two non-coordinating dinitramide counterions in the molecular unit (Figure 13). All rings are in *anti* conformation to the propyl chain, which enables the linkage of one transition metal to six other copper(II) ions and leads to a tightly packed three-dimensional network with a density of  $1.711 \text{ g cm}^{-3}$ . The complex crystallizes in form of blue platelets in the monoclinic space group  $C2/c$  with 8 formula units per unit cell.



**Figure 13** Coordination environment of the anhydrous copper(II) dinitramide complex **15**. Selected bond lengths (Å): Cu2–N16 2.3861(16), Cu2–N20 2.0437(14), and Cu2–N24 2.004(2); selected bond angles (°): N16–Cu2–N20 85.55(6), N16–Cu2–N24 90.87(7), and N20–Cu2–N24 88.81(7). Symmetry codes: (i) –x, 1–y, –1–z; (ii) x, y, –1+z; (iii) –0.5–x, 0.5–y, –1–z.

### Sensitivities and thermal stability

Endothermic signals such as melting, dehydration or loss of aqua ligands, as well as other critical temperatures of all compounds were investigated by differential thermo analysis (DTA) with a heating rate of  $\beta = 5 \text{ °C min}^{-1}$ . The determined onset temperatures are listed in Table 2. DTA plots and additional details of the coordination compounds **1–3**, **8** and **10–15** are displayed in Figures S11–13 in the Supporting Information. The ditetrazole ligands melt at  $45 \text{ °C}$  (2,2-dtp),  $50 \text{ °C}$  (1,2-dtp) and  $126 \text{ °C}$  (1,1-dtp). Higher melting points are observed the more N1 substitution is present at the heterocycle, which is in accordance with literature observed values.<sup>47</sup> All complexes (except **10** and **15**) show excellent exothermic decomposition temperatures with values greater than  $210 \text{ °C}$ . The thermal stabilities of the investigated compounds exceed in most cases the temperatures observed for the uncoordinated ligands. The silver(I) perchlorate **10** and copper(II) dinitramide **15** complexes show the lowest exothermic decomposition temperatures of all examined compounds with values of  $186 \text{ °C}$  (**10**) and  $154 \text{ °C}$  (**15**), respectively. The poor stability toward heat of dinitramide containing compounds is a well-known issue and has already been described in the literature.<sup>48</sup>

**Table 2.** Thermal stability measurements of **1–15** by DTA.

	$T_{\text{endo.}} (\text{°C})^{\text{[a]}}$	$T_{\text{exo.}} (\text{°C})^{\text{[b]}}$
<b>1,1-dtp</b> • $\text{H}_2\text{O}$ ( <b>1</b> )	68 (– $\text{H}_2\text{O}$ ), 126	205
<b>1,2-dtp</b> ( <b>2</b> )	50	212
<b>2,2-dtp</b> ( <b>3</b> )	45	246
$[\text{Mn}(1,1\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>4</b> )	–	243
$[\text{Fe}(1,1\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>5</b> )	–	234
$[\text{Co}(1,1\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>6</b> )	–	255
$[\text{Ni}(1,1\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>7</b> )	–	297
$[\text{Cu}(1,1\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>8</b> )	–	231
$[\text{Zn}(1,1\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>9</b> )	–	253
$[\text{Ag}(1,2\text{-dtp})](\text{ClO}_4)$ ( <b>10</b> )	–	185
$[\text{Cu}(1,2\text{-dtp})_3](\text{ClO}_4)_2$ ( <b>11</b> )	–	222
$[\text{Cu}(\text{H}_2\text{O})_2(2,2\text{-dtp})_2](\text{ClO}_4)_2$ ( <b>12</b> )	132 (– $\text{H}_2\text{O}$ )	257
$[\text{Cu}(\text{TNR})(1,1\text{-dtp})] \cdot \text{H}_2\text{O}$ ( <b>13</b> )	88 (– $\text{H}_2\text{O}$ )	248
$[\text{Cu}(\text{H}_2\text{O})_2(1,1\text{-dtp})_2](\text{CDNM})_2$ ( <b>14</b> )	93 (– $\text{H}_2\text{O}$ )	212
$[\text{Cu}(1,1\text{-dtp})_3](\text{DN})_2$ ( <b>15</b> )	–	153

onset temperatures at a heating rate of  $5 \text{ °C min}^{-1}$  [a] endothermic peak, which indicates melting, dehydration or loss of aqua ligands; [b] exothermic peak, which indicates decomposition.

The observation of endothermic signals, which indicate melting, dehydration or loss of aqua ligands for the compounds **1–3** and **12–14** match perfectly to the described structural composition. The outstanding thermal stabilities of most complexes can be explained by the formation of extended structures (MOFs) and the related strengthening of the scaffold within the coordination compounds. In contrast, complex monomers based on relatively volatile ligands suffer from a high vaporization tendency resulting in earlier decomposition after reaching the critical temperature.<sup>6</sup> Therefore, two selected complexes **6** and **8** were checked by thermal gravimetric analysis (TGA, Figure 14). The theory of a higher stability of coordination polymers could be confirmed. Both polymeric compounds showed no weight loss until

decomposition during heating. The exothermic decomposition temperatures of the metal(II) 1,1-dtp perchlorate complexes **4–9**, depicted in Figure 15, rise in the following order: Cu<sup>2+</sup> (231 °C) < Fe<sup>2+</sup> (234 °C) < Mn<sup>2+</sup> (243 °C) < Zn<sup>2+</sup> (253 °C) < Co<sup>2+</sup> (255 °C) < Ni<sup>2+</sup> (297 °C). A similar trend has been described in the literature for metal(II) perchlorate complexes bearing 1-methyl-5H-tetrazole as ligand.<sup>6</sup>

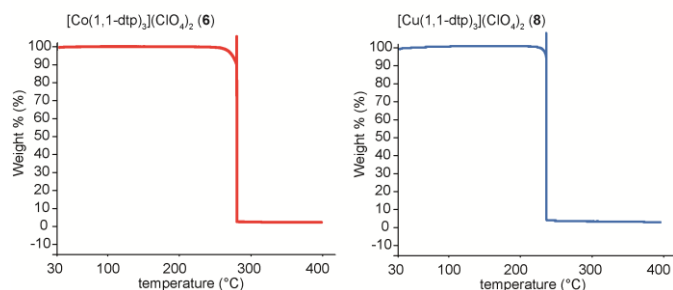


Figure 14 TGA measurements of the selected coordination compounds **6** and **8** at a heating rate of 5 °C min<sup>-1</sup>.

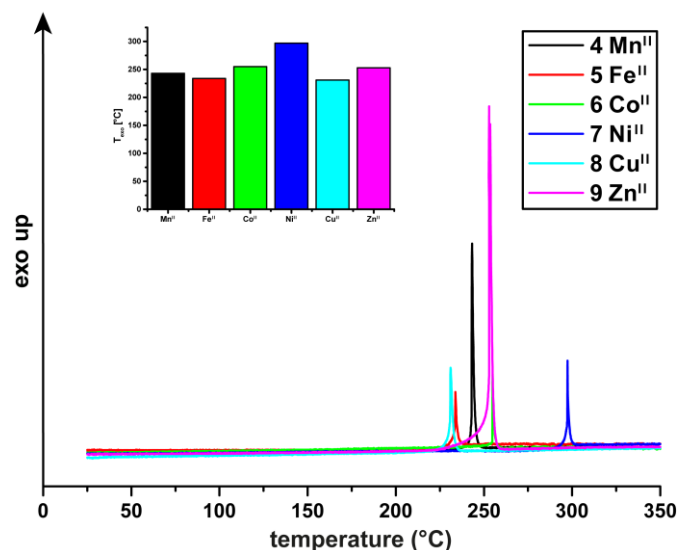


Figure 15 DTA plot (5 °C min<sup>-1</sup>) comparison of the 1,1-dtp containing metal(II) perchlorate complexes **4–9**.

The nitrogen substitution pattern of the ditetrazoles has a strong influence on the exothermic decomposition temperature, which can be observed for the uncoordinated ligands **1–3** and their corresponding copper(II) perchlorate complexes (Figure S12). Comparison of 1,1-dtp complexes with copper(II) as metal, but varying anions showed again the relevance and dependency of different coordination environments for the thermal stabilities (Figure S13).

The sensitivities toward impact and friction were measured according to BAM standard methods together with the electrostatic discharge sensitivity for all compounds. Further, the compounds have been categorized in compliance with the “UN Recommendations on the Transport of Dangerous Goods” using the determined values. An outline of the sensitivities is given in Table 3. The uncoordinated ditetrazole ligands **1–3** can be described as “insensitive” with values greater than 40 J for

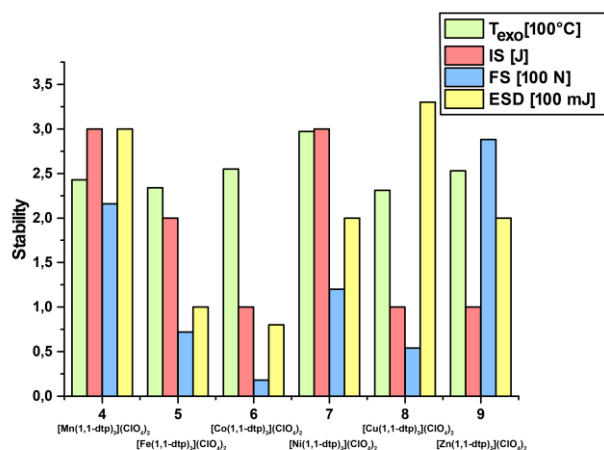
impact, greater than 360 N for friction and ESD values between 0.15–1.50 J. All perchlorate complexes **4–12** (except **10** with a value of 8 J) can be considered as very sensitive against impact (1–3 J) and vary from sensitive to very sensitive toward friction (16–288 N).

Table 3. Sensitivities toward impact, friction and ESD of **1–15**.

	IS (J) [a]	FS (N) [b]	ESD (J) [c]
<b>1</b>	> 40	> 360	1.35
<b>2</b>	> 40	> 360	1.50
<b>3</b>	> 40	> 360	0.15
<b>4</b>	3	216	0.30
<b>5</b>	2	72	0.10
<b>6</b>	1	18	0.08
<b>7</b>	3	120	0.20
<b>8</b>	1	54	0.33
<b>9</b>	1	288	0.20
<b>10</b>	8	16	0.15
<b>11</b>	1.5	18	0.10
<b>12</b>	1.5	64	0.30
<b>13</b>	10	> 360	0.50
<b>14</b>	10	> 360	0.50
<b>15</b>	3	> 360	0.70

determined at a grain size < 100 μm; [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 ≥ 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.

Application of metal(II) salts with oxidizing anions like trinitrorescorinates, cyanodinitromethanides or dinitramides in combination with endothermic ligands usually caused intensified sensitivities toward various stimuli like impact, friction and ESD (impact: 3–10 J; friction: > 360 N; ESD: 0.50–0.70 J). Inclusion of crystal water molecules or aqua ligands on the other hand lowered the performance and lead to a lower sensitivity under most circumstances. The sensitivity toward impact of the [M<sup>II</sup>(1,1-dtp)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> coordination compounds (Figure 16) increases in the following order: Mn<sup>2+</sup> (3 J) ≈ Ni<sup>2+</sup> (3 J) < Fe<sup>2+</sup> (2 J) < Zn<sup>2+</sup> (1 J) ≈ Cu<sup>2+</sup> (1 J) ≈ Co<sup>2+</sup> (1 J) and in the following order against friction: Zn<sup>2+</sup> (288 N) < Mn<sup>2+</sup> (216 N) < Ni<sup>2+</sup> (120 N) < Fe<sup>2+</sup> (72 N) < Cu<sup>2+</sup> (54 N) < Co<sup>2+</sup> (18 N). Comparable results have been described in the literature in connection with 1,5-diaminotetrazole and 1-methyl-5H-tetrazole containing ECC.<sup>6,49</sup> In addition, fine-tuning of the complexes stability can be achieved through the appropriate choice of the implemented dtp ligands or oxygen-rich anions (Figure S14/15). The presented copper(II) perchlorate complexes show promising characteristics by having manageable sensitivities, which makes them highly suitable as laser ignitable substances in modern initiation devices.



**Figure 16** Comparison of the stabilities of the 1,1-dtp containing metal(II) perchlorate complexes 4–9.

Initiation capability tests by hot plate and hot needle were performed for the most promising compounds **8**, **11** and **12**. All investigated complexes showed deflagrations in both tests and no detonations indicating valuable compounds with moderate sensitivities and performances for laser ignition experiments (Figure 17 and Figure S16–18). More details on the procedures can be found in the experimental section.



**Figure 17** Moment of deflagration of compound **8** during the hot plate test shown as a sequence.

### Toxicity assessment

In order to determine the toxicological impact of complexes with isomeric propyl-linked ditetrazoles, the uncoordinated free ligands (**1**, **2** and **3**), as well as their corresponding copper(II) complexes (**8**, **11** and **u**) were tested. The toxicity determinations were carried out with a LUMI-Stox 300 spectrometer obtained by HACH LANGE GmbH, as described by the provider. A ten-point dilution series was prepared according to DIN/EN/ISO 11348 (without G1 level) with a known weight of the compounds and a 2% NaCl stock solution.<sup>50</sup> The measurements were performed at a temperature of 15 °C starting with the determination of the bioluminescence of untreated reactivated *Vibrio fischeri* NRRL-B-11177 bacteria strains. The bioluminescence again is

determined after 15 and 30 minutes exposure time with a specific amount of component. At the concentration level where the bioluminescence is decreased by 50%, the EC<sub>50</sub> (effective concentration) value is obtained. Compounds can be classified as non-toxic according to their EC<sub>50</sub> values (non-toxic > 1.00 g/L; toxic 0.10–1.00 g/L; very toxic < 0.10 g/L).<sup>51</sup>

**Table 4.** Experimental EC<sub>50</sub> values for the uncoordinated free ligands **1–3** in comparison to their respective copper(II) perchlorate complexes **8**, **11** and **12**.

Compound	EC <sub>50</sub> (15 min)	EC <sub>50</sub> (30 min)
	[g/L]	[g/L]
<b>1,1-dtp • H<sub>2</sub>O (1)</b>	13.90	10.30
<b>1,2-dtp (2)</b>	0.81	0.79
<b>2,2-dtp (3)</b>	0.36	0.36
<b>[Cu(1,1-dtp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (8)</b>	0.44	0.35
<b>[Cu(1,2-dtp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (11)</b>	0.64	0.44
<b>[Cu(H<sub>2</sub>O)<sub>2</sub>(2,2-dtp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (12)</b>	0.34	0.28

As shown in Table 4, the half-maximum effective concentrations of the propyl-linked ditetrazoles varies considerably. Compound **1** has an EC<sub>50</sub> value of 10.30 g/L after 30 minutes and can be considered as non-toxic. It is interesting to note that in contrast to ligand **1**, the isomeric compounds **2** (0.84 g/L) and **3** (0.36 g/L) show increased toxicities by having only a slightly different substitution pattern. Similar values have been observed for all copper(II) complexes, which is not surprising due to the known toxicity toward microorganisms.<sup>52</sup> It also became apparent that the ditetrazole **3** and complexes containing this ligand are more toxic toward *Vibrio fischeri*. Copper(II) compound **12** is the most toxic complex, even though it forms complexes with two aqua ligands and two ditetrazole ligands instead of three ditetrazole ligands (compounds **8** and **11**). Furthermore, the toxicity values of **8**, **11** and **12** are in a proportional range of other copper(II) perchlorate complexes, but slightly less toxic compared to already known 1-methyl-5*H*-tetrazole analogues.<sup>6</sup> This could lead to a general trend that 2-alkylated 5-*H*-tetrazoles are more toxic than their 1-alkylated analogues.

### Laser ignition tests

Over the past few years, many new laser ignitable materials based on energetic coordination compounds have been explored and developed by several researchers all over the world.<sup>33,53–55</sup> Initiation by laser has various benefits in comparison to classical ignition methods like thermal initiation (bridge wire) or mechanical stimuli (e.g. stab initiation). Since high sensitivities against usual stimuli are no longer needed, almost insensitive highly energetic compounds can be used, which can reduce undesired initiations and allows safer processing. The “green” laser ignitable explosives presented in this study feature all desired characteristics like high performance, superior thermal stability, moderate sensitivities and no environmental impact. Approximately 15 mg of the carefully pestled complex to be investigated was filled into a transparent plastic cap (PC), pressed with a pressure force of 1 kN and sealed by a UV-curing adhesive. The laser initiation experiments were performed with a 45 W InGaAs laser diode

operating in the single-pulsed mode. The diode is attached to an optical fiber with a core diameter of 400  $\mu\text{m}$  and a cladding diameter of 480  $\mu\text{m}$ . The optical fiber is connected via a SMA type connector directly to the laser and to a collimator. This collimator is coupled to an optical lens, which was positioned in its focal distance ( $f = 29.9$  mm) to the sample. The lens is shielded from the explosive by a sapphire glass. The confined samples were irradiated at a wavelength of 915 nm, a voltage of 4 V, a current of 8 A and varying pulse lengths (0.1 ms or 15 ms). The combined current and pulse length result in an energy output of about 0.20 mJ (0.1 ms/8 A) and 30 mJ (15 ms/8 A). Only selected complexes with promising characteristics and moderate sensitivities were tested showing different behaviors upon laser irradiation depending on the metal(II)/anion combination. An overview of the experimental results is given in Table 5.

**Table 5.** Results of the laser ignition tests.

	0.1 ms/8 A	1 ms/8 A	15 ms/8 A
<b>5</b>	det.	—	—
<b>6</b>	x	x	det.
<b>7</b>	—	—	dec.
<b>8</b>	det.	—	—
<b>9</b>	—	—	x
<b>11</b>	det.	—	—
<b>12</b>	det.	—	—
<b>13</b>	—	—	deflag.
<b>14</b>	—	—	dec.
<b>15</b>	—	—	deflag.

(—: not tested, x: no ignition, dec.: decomposition, deflag.: deflagration, det.: detonation). Operating parameters: current  $I = 8$ –9 A; voltage  $U = 4$  V; theoretical maximal output power  $P_{\text{max}} = 45$  W; theoretical energy  $E_{\text{max}} = 0.20$ –30 mJ; wavelength  $\lambda = 915$  nm; pulse length  $\tau = 0.1$ –15 ms.

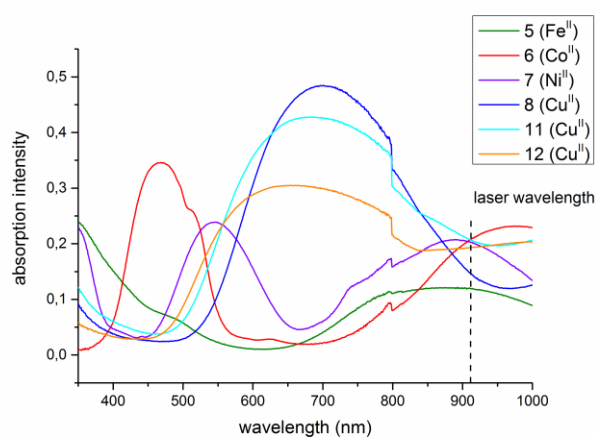
The zinc(II) complex **9** was the only compound investigated, which showed no reaction after laser irradiation. All other complexes examined could be initiated showing decompositions for **7/14**, deflagrations for **13/15** and detonations for **5, 6, 8, 11** and **12** (Figure 18 and Figure S19–22). Various laser initiation thresholds could be observed for the varying coordination compounds, which exhibit similar sensitivities toward mechanical stimuli, but showed different responses under the employed laser settings. The iron(II) and copper(II) perchlorate complexes **5, 8, 11** and **12** detonated at the lowest possible initiation energy available in the parameters of the laser device and could be promising candidates in future laser initiation systems based on their outstanding initiation capabilities and highly practicable sensitivities.



**Figure 18** Moment of detonation of complex  $[\text{Fe}(1,1\text{-dtp})_3](\text{ClO}_4)_2$  (**5**) in the laser initiation experiment.

### UV-Vis spectroscopy

The solid-state UV-Vis spectra of all coordination compounds **4–15** were recorded in the wavelength region of 350–1000 nm to acquire a better understanding and get a deeper insight into the laser initiation process (Figure 17 and Figure S23). Observed optical characteristics are collected and listed in Table 6. The investigated complexes showed characteristic transitions in the near-infrared, visible and UV region responsible for the complementary colours and typical for the related transition metal. Observed absorptions can be primarily designated to the d-d transitions of the corresponding metals and are largely dependent on the inserted metal(II), anion and ligand (Figure 19).



**Figure 19** UV-Vis spectra in the solid state of selected complexes. The step in the absorption intensity at 800 nm in the spectra is caused by a detector change. The UV-Vis spectra have only qualitative character.

As assumed initially, no absorptions could be observed for the  $d^5$  manganese(II) compound **4** and the two  $d^{10}$  complexes with zinc(II) **9** and silver(I) **10**. Additional strong  $n\text{-}\pi^*$  transitions from the UV to the blue visible region (Figure S23) could be detected in the copper(II) complexes **13–15** caused by the nitro group containing anions (trinitroresorcinate, cyanodinitromethanide, dinitramide).

Many uncertainties of the fundamental basis of the laser initiation process (e.g. electronically, thermally or combined) have not been clarified yet and are still questionable.<sup>34,56,57</sup> Solely looking at the absorption of the coordination compounds at the laser wavelength of 915 nm one could conclude a possible direct interrelationship with the laser initiation capability once all complexes could be ignited. The initiation ability of energetic materials by laser does not only depend on the absorption at the relevant wavelength but also other factors like the electronic structure or the metal center surrounding. It can be assumed that reaction of the coordination compounds after irradiation by laser light may occur when energetic materials exhibit high sensitivities toward mechanical stimuli. Future studies are necessary to gain further insights into the laser initiation process, which

should cover the effect of the compounds composition (metal, anion or ligand) and investigate the nature of the mechanism.

**Table 6.** Observed optical characteristics of 4–15.

	M	color	$\lambda_{d-d}$ [a]	$\lambda_{915}/\lambda_{d-d}$ [b]
4	Mn <sup>II</sup>	colorless	—	—
5	Fe <sup>II</sup> (hs)	yellow	893	0.97
6	Co <sup>II</sup>	orange	468, 982	0.61
7	Ni <sup>II</sup>	purple	547, 891	0.84
8	Cu <sup>II</sup>	blue	701	0.30
9	Zn <sup>II</sup>	colorless	—	—
10	Ag <sup>I</sup>	colorless	—	—
11	Cu <sup>II</sup>	blue	688	0.48
12	Cu <sup>II</sup>	blue	654	0.63
13	Cu <sup>II</sup>	green	390 [c], 696	1.00
14	Cu <sup>II</sup>	blue	389 [c], 624	0.51
15	Cu <sup>II</sup>	blue	377 [c], 630	0.41

[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.

## Conclusions

Three isomeric ditetrazolylpropanes (1,3-di(tetrazol-1-yl)propane (1,1-dtp), 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (2, 1,2-dtp) and 1,3-di(tetrazol-2-yl)propane (3, 2,2-dtp), differing, only in the nitrogen substitution pattern at the tetrazole, were prepared and purified in a straightforward one-step synthesis through alkylation of 1,5H-tetrazole. Different synthetic strategies were applied and the influence of various preparative parameters on the reaction product composition systematically investigated. Analysis and comparison of these procedures resulted in deep insights into the effect on the yield and ratio of the isomers from different solvent systems, various organic/inorganic bases, the influence of a phase transfer catalyst and a distinct work-up method. Obtained endothermic n-propyl linked ditetrazoles were exhaustively characterized by various methods including toxicity assessments, X-ray studies and heteronuclear <sup>15</sup>N NMR spectroscopy. Toxicity determinations toward aquatic life of the free uncoordinated ligands together with the promising related copper(II) perchlorate complexes showed that 1-alkylated species are less toxic than their 2-alkylated isomers. The concept of ECC is an excellent, fair and simple approach in order to find environmentally friendly primary explosives or materials applicable for laser ignition experiments with reasonable sensitivities. Laser initiation experiments with 1,2-di(tetrazol-5-yl)ethane (1,1-dte) based transition metal(II) complexes have shown promising results in the past but were too sensitive for any application. As a logical consequence, ditetrazolylpropane ligands with higher carbon contents especially the N1,N1-substituted ditetrazole (1,1-dtp) were now implemented into the corresponding coordination compounds in order to increase the stability of the new energetic materials. The present contribution covers the synthesis, characterization and comparison of 12 new eco-

friendly energetic coordination compounds (ECC) based on three different isomeric propyl-linked ditetrazoles, which differ drastically in their coordination pattern. Complexation of the ligands leads to intramolecular reorientation of the ditetrazole molecules and enables the formation of polymeric chains. Optical as well as energetic properties of the highly functional complexes were accurately tuned by the careful selection of the varying metal(II) salts and also the appropriate choice of the isomers. Synthesized coordination compounds consist of a first-row transition metal(II) (Mn, Fe, Co, Ni, Cu, Zn), several different anions (ClO<sub>4</sub><sup>-</sup>, TNR<sup>2-</sup>, CDNM<sup>-</sup>, DN<sup>-</sup>) and one of the three isomeric ditetrazoles. Approaches utilizing Ag(I) as metal center failed with the exception of coordination compound 10 with 1,2-dtp as ligand. In order to form thermally stable materials, non-volatile bridging bidentate ditetrazole ligands were implemented into the complexes to establish highly stable multidimensional polymeric structures (MOFs). Through this strategy extraordinary exothermic decomposition temperatures could be achieved for all complexes up to a very impressive 297 °C for compound 7, which were partly checked and confirmed by thermal gravimetric analysis (TGA). The powerful water-free nature of the majority of the energetic complexes was revealed through single crystal X-ray experiments of all compounds (except complex 7), which allowed interesting correlations between the crystal structures and their stabilities toward mechanical stress (highest sensitivities for cobalt(II) perchlorate complex 6). Laser initiation tests, which were performed at a wavelength of 915 nm showed detonations for the most promising iron(II) and copper(II) complexes 5, 8, 11, 12 at the lowest configurable laser setup energy input (0.2 mJ). The successful initiations proved the suitability of these high performing and thermal stable candidates for future laser initiation systems, which can be easily synthesized from inexpensive chemicals in a simple, inexpensive and upscalable reaction.

## Conflicts of interest

“There are no conflicts to declare”.

## Acknowledgements

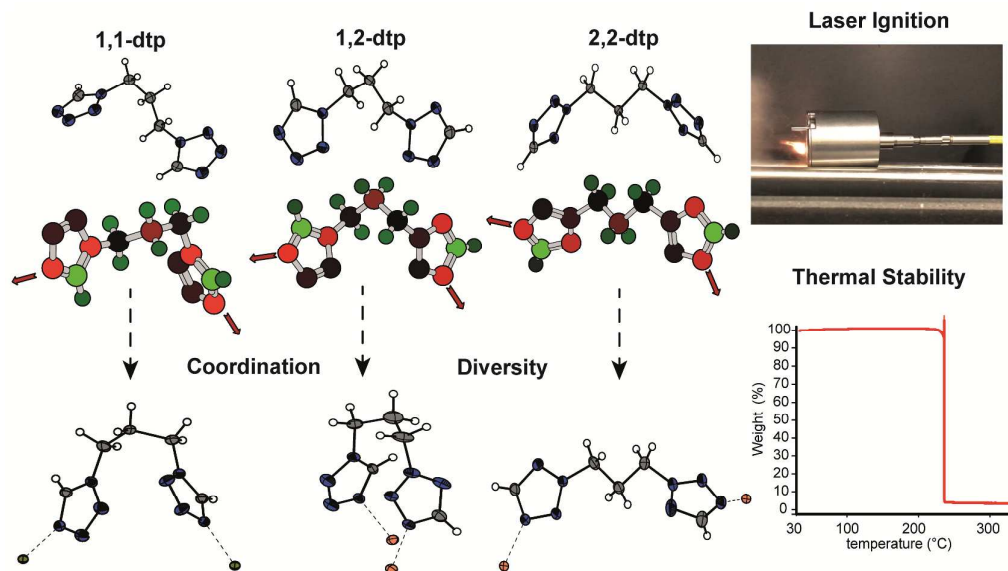
Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. ONR.N00014-16-1-2062. The authors want to thank Stefan Huber for sensitivity measurements, Mr. Josh Bauer for proofreading and Prof. Dr. Konstantin Karaghiosoff for the measurement of various <sup>15</sup>N NMR spectra.

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## Graphical Abstract



A series of highly functional new energetic coordination compounds (ECC) were prepared by using three different propyl-linked ditetrazolypropane isomers. Their physico-chemical properties can easily be tuned by variation of the metal(II) salt and for the first time through exchange of an isomeric heterocycle building block. The synthesized transition metal complexes showed moderate sensitivities toward mechanical stimuli and excellent thermal stabilities making them to promising candidates for the use in optical laser initiation systems.