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Investigation of the Capability of Azidotriazoles as Primary Explosives

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Erklärung

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The Road goes ever on and on
Down from the door where it began.
Now far ahead the Road has gone,
And I must follow, if I can,
Pursuing it with eager feet,
Until it joins some larger way
Where many paths and errands meet.
And whither then? I cannot say.

---

from J. R. R. Tolkien's *The Lord of the Rings*

Table of Contents

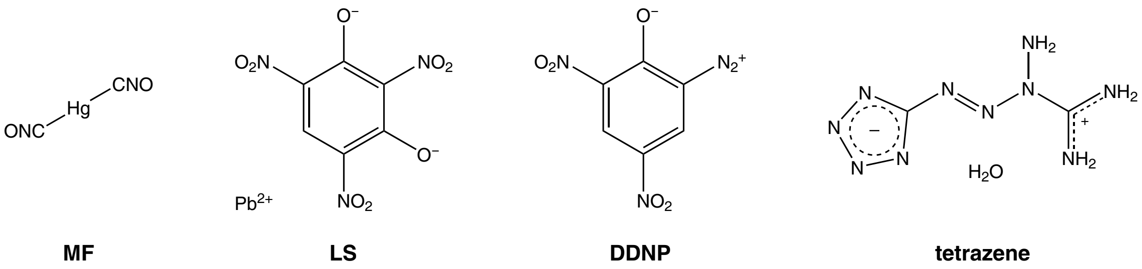
Introduction

1.1 Classification of Energetic Materials

According to the ASTM International (formerly called American Society for Testing and Materials) definition, an energetic material is a substance, or a mixture of substances which contains both oxidizer and fuel, and reacts readily with the release of large amounts of energy and gas, without the need for external reaction partners (e.g. atmospheric oxygen), resulting in an explosion.[1] However, it should be noted that there are several energetic materials for which the reaction does not lead to an increase in pressure due to the formation of exclusively solid and liquid products (like the mixture of sulfur hexafluoride and lithium in chemical thermal propulsion systems).

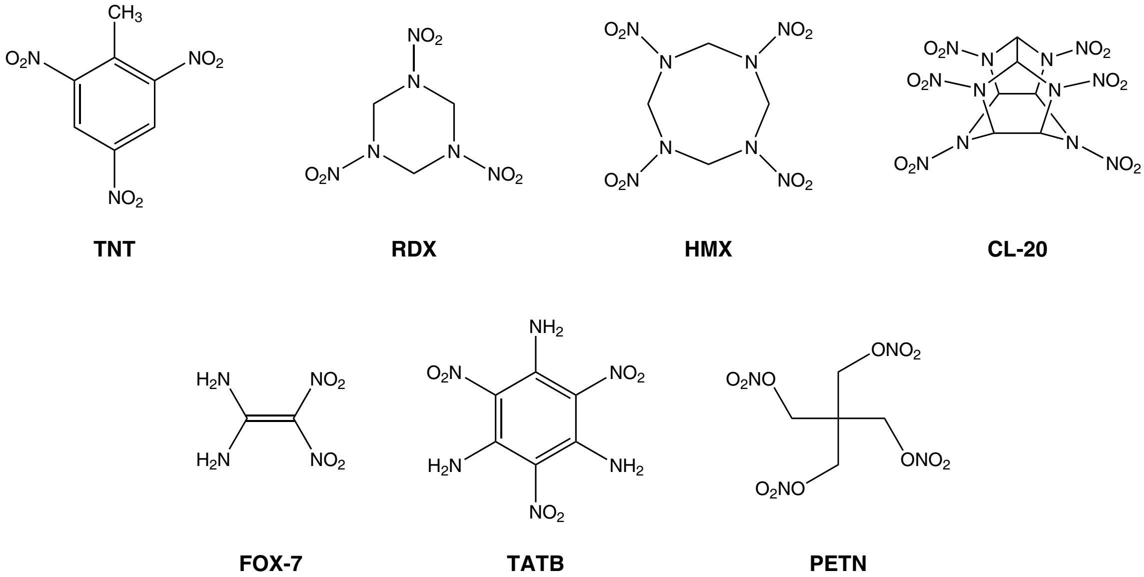
Depending on their type of initiation and energetic behavior, energetic materials can be divided into primary explosives, secondary explosives, pyrotechnics and propellants.

Primary Explosives These are the most sensitive and most easily initiated energetic materials and the focus of this work. Unlike secondary explosives, they are able to detonate upon thermally induced decomposition even in an unconfined state. This is the result of the deflagration-to-detonation transition (DDT) after a simple initiating impulse (SII) in which the subsonic heat transfer based decomposition becomes so fast that it transforms into a supersonic shock wave.[2] Various non-explosive outer stimuli can serve as SII, mainly heat, impact, friction or an electric spark. The impact sensitivity (IS) of these compounds is usually less than 4 J, the friction sensitivity (FS) is less than 10 N and the detonation velocity is in the range of 3500 to 5500 $\mathrm{m\,s^{-1}}$.[3] The resulting shock wave of the detonation can then be used to initiate a secondary explosive. Primary explosives can be further divided into those that detonate virtually immediately like lead azide (LA) or silver azide and those which undergo a measurable DDT like mercury fulminate (MF), lead styphnate (LS), 2-diazo-4,6-dinitrophenol (DDNP) and tetrazene.[4]



MF **LS** **DDNP** **tetrazene**

Figure 1.1: Molecular structures of MF, LS, DDNP and tetrazene.



TNT RDX HMX CL-20

FOX-7 TATB PETN

Figure 1.2: Molecular structures of TNT, RDX, HMX, CL-20, FOX-7, TATB and PETN.

Secondary Explosives Contrary to primary explosives these are unable to detonate when subjected to a SII when unconfined but rather need a shock wave as initiating source, usually that of a primary explosive. However, their performance is much higher with detonation velocities usually around 6500 to $9000\,\mathrm{m\,s^{-1}}$, coupled with much lower sensitivities (IS more than 4 J and FS more than 50 N).[3] The oldest of the currently employed secondary explosives is the melt castable 2,4,6-trinitrotoluene (TNT). It was first prepared in 1863 by Julius Wilbrand,[5] but only found wide use as an explosive during the course of World War I, such as in the form of amatol[6] (e.g. 60 % TNT and 40 % ammonium nitrate). The currently most employed secondary explosive, which also serves as benchmark for new developments, is 1,3,5-trinitro-1,3,5-triazinane (RDX). First prepared in 1898 by Georg Friedrich Henning,[7] it found wide use during and after World War II, such as in the form of torpex[6] (e.g. 42 % RDX, 40 % TNT and 18 % aluminum) or the novel IMX-104[8] (RDX, 2,4-dinitroanisole and 3-nitro-1,4*H*-1,2,4-triazol-5-one). Other important examples are the two rather sensitive secondary explosives 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX, the higher homologue of RDX) and 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20), which are the most powerful compounds currently in use, and insensitive explosives like 1,1-diamino-2,2-dinitroethene (FOX-7) or 2,4,6-triamino-1,3,5-trinitrobenzene (TATB). A sub-class of secondary explosives are booster explosives like pentaerythritol tetranitrate (PETN) which have a slightly lower performance but are easier to initiate. Secondary explosives are thus used as the main charge of demolition devices (torpedoes, bombs, mining charges, etc.) and are initiated by the so called detonators, which generate the required shock wave. The sequence of primer (usually a pyrotechnic mixture, often containing a primary explosive)

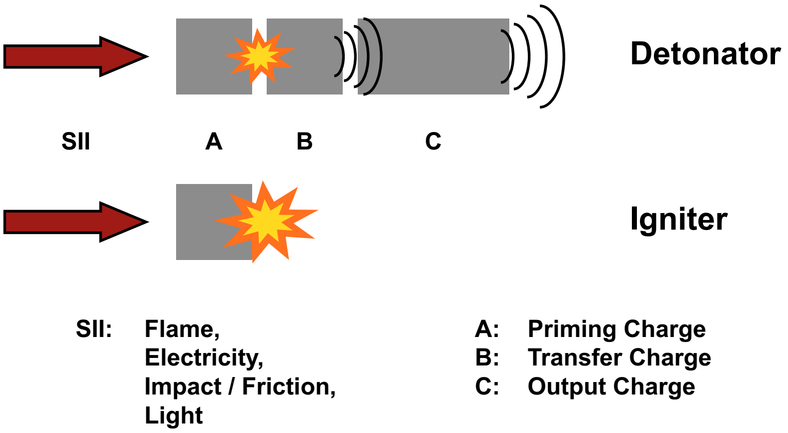
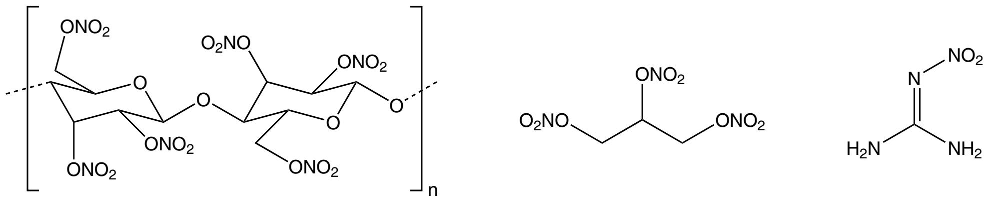


Figure 1.3: Schematic representation of the initiating train of a detonator (top), in comparison to an igniter (bottom). Priming charge: pyrotechnic mixture, often containing a primary explosive. Transfer charge: primary explosive. Output charge: secondary explosive.

which generates a flame, primary explosive which generates a shock wave and secondary explosive which further amplifies the shock wave is called an initiating train (see figure 1.3 for an illustration).[4]

Pyrotechnics Literally being the art of fire (from greek *pyro* “fire” and *tekhnikos* “made by art”), pyrotechnics are most famously known in the form of fireworks and signal flares. Contrary to primary and secondary explosives, which contain the oxidizer and the fuel in a single molecular unit, pyrotechnics are usually a mixture of different substances. They can additionally contain additives for smoke, noise and bright light generation, for example in cover providing smoke grenades and disorientation causing stun grenades (“flashbangs”), but also colorants for regular firework usage. Another important use is as initiators in or for explosive charges in the form of heat generating pyrotechnics. Examples are the electric match type blasting cap in which a pyrotechnical mixture is heated up and thus ignited by an electric current and then proceeds to initiate a primary explosive, or the gasless delay fuse in hand grenades. Typical oxidizers are perchlorates and nitrates (and chromates in delay fuses) of potassium and barium, while typical fuels are boron and silicon or metals like magnesium, titanium and zirconium.[3]

Propellants The most characteristic feature of this group is the controlled deflagration which does not propagate into a detonation. Black powder (a variable mixture of about 75 % potassium nitrate, 10 % sulfur and 15 % charcoal) is the first and probably most famous energetic material and propellant. The group can be further divided into gun propellants and rocket propellants. Black powder was the first gun propellant in both large caliber guns (cannons) and handguns (arquebus and later the musket), but has been



NC NG NQ

Figure 1.4: Molecular structures of NC, NG and NQ.

largely replaced due to its low efficiency by single, double and triple base gun propellants on the basis of nitrocellulose (NC), nitroglycerin (NG) and nitroguanidine (NQ).[3] Modern composite gun propellants consist of a high explosive like RDX (around 20 to 60 %), often a polymeric binder, plasticizers and further additives for example as stabilizers or to remove corrosive and poisonous gases.[9–11] Rocket propellants on the other hand, which can be solid or liquid, do not accelerate a separate projectile but act as the propulsion system for a manned or unmanned projectile. In general the main difference between these two propellant types is the fact that gun propellants are best described with an isochoric combustion (rapid increase in pressure to propel the charge out of the barrel) and rocket propellants with an isobaric combustion (continuous expansion of the gaseous decomposition products into the atmosphere or space). Solid propellants usually consist of ammonium perchlorate as oxidizer, aluminum as fuel and hydroxyl-terminated polybutadiene (HTPB) as binder.[3] Liquid propellants can be hypergolic “mixtures” like dinitrogen tetroxide and monomethylhydrazine (MMH) which spontaneously and immediately (less than 20 ms) react when brought together, or cryogenic mixtures like hydrogen and oxygen.[3] Liquid monopropellants, with a catalyst induced decomposition like hydrazine, are also in use.[3]

1.2 Primary Explosives

Mercury fulminate (MF), which has already been discovered around the 17th century by alchemists, was first patented at the beginning of the 19th century for use in priming mixtures, but almost 60 years went by until Alfred Nobel invented his “Fulminate Blasting Caps” for the initiation of his NG based dynamite.[4] In the following years, a mixture containing 13.7 % MF, 41.5 % potassium chlorate, 33.4 % antimony trisulfide, 10.7 % powdered glass and 0.7 % gelatin glue emerged as the most widespread priming mixture for percussion primers.[12] While potassium chlorate is the main oxidizer, MF enables a reliable initiation. Antimony trisulfide serves as fuel and the glass powder as sensitizer. Although the preparation is quite easy and cheap from elemental mercury, nitric acid and ethanol, one of its major drawbacks is the high toxicity of mercury.[13]

Even at the beginning of the 20th century, alternatives were already being investigated and tested. Lead azide (LA) and lead styphnate (LS) emerged as the most successful replacements, with LA still being by far the most frequently used primary explosive even today. Examples for priming compositions are the rust-preventing chlorate-free SINOXID (*sine oxid*: LS, tetrazene, barium nitrate, lead dioxide, antimony trisulfide and calcium silicide) from 1928,[6,14] its lead-free successor SINTOX (*sine toxico*: DDNP, terazene, zinc peroxide and titanium),[6,14] or the NOL-130 stab mix (basic LS, LA, tetrazene, barium nitrate and antimony trisulfide), which is, for example, used in the M55 stab detonator.[15,16] The major drawback of LA and LS is again toxicity, especially at indoor shooting ranges.[17] Lead is highly toxic to many organs and tissues including the heart, bones, intestines, kidneys, and the nervous system.[18]

It is therefore of major interest to replace all kinds of lead containing compounds,[19] and less toxic primary explosives are therefore highly sought after.[20–22] A metal-free potential primary explosive is the binary C-N compound 2,4,6-triazido-1,3,5-triazine (TTA) which had already been investigated and patented in 1921,[23,24] and is currently (again) investigated for at least partial LA replacement in the NOL-130 stab mixture.[16] A potential LS replacement with an environmentally benign metal is the potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (KDNP).[25] One of the most thoroughly investigated class of compounds in the previous century are the derivatives of 1*H*-tetrazole.[2,4,21,26–36] The first derivative which found use as an explosive and is currently still by far the most widespread is 1-(5-tetrazolyl)-3-guanyltetrazene hydrate (tetrazene in short), first prepared in 1910.[26] Due to its rather poor initiating capability it is mostly used as a reliable sensitizer. For example the addition of 2 % tetrazene to LA lowers the stab initiation energy from 1000 mJ to 3 mJ.[27] Unfortunately, it suffers from a rather low decomposition temperature around 140 °C. Other investigated derivatives are most notably the metal salts of 5-nitro-2*H*-tetrazole,[2,4,28] 5-azido-1*H*-tetrazole,[4,29] 5-chloro-1*H*-tetrazole,[4,30] bis(1*H*-tetrazol-5-yl)amine,[31] 1,2-bis(1*H*-tetrazol-5-yl)diazene,[4,32] and 1,3-bis(1*H*-tetrazol-5-yl)triazene.[33] Notable as a potential "green" primary explosive is copper(I) 5-nitrotetrazolate (DBX-1),[28] currently discussed as a potential drop-in replacement for LA based priming compositions.[34] 5-Nitro-2*H*-tetrazole also serves as ligand in tetraammine-*cis*-bis(5-nitrotetrazolato-N^2)cobalt(III) perchlorate (BNCP).[35] BNCP is not only suitable as a rather "green" primary explosive but it can be easily initiated by laser irradiation.[36] While perchlorates are apparently not seen as a large problem in many countries worldwide,[4] they are deemed unsuitable in the USA due to the toxicity as a result of the competition of the perchlorate ion with iodine in the thyroid gland which can cause, for example, growth and development dysfunctions.[37–39] Although reportedly perchlorate pollution is far less of a problem for the human health than usually being accused of,[40] it is still rather problematic as a priming component in weapon systems owing to potential corrosion problems (the same reason why the use of potassium chlorate in percussion primers has been abandoned in the first place). This illustrates the problem that most of the main components in priming compositions are either unfavorable for the user (toxic) or the device (corrosion), although this is less of a problem in bombs and missiles in which the device is destroyed anyway.

1.3 Primary Explosives as Initiators

The first firearms were based on black powder as gun propellant and used a burning fuse in the form of the unwieldy matchlock (15th to 17th century) as initiating device. Flame was similarly used in cannons, again to ignite black powder. The matchlock was succeeded by the flintlock (17th to 19th century) which produced flame sparks from a spring operated flint striking on a metal surface, and finally by the percussion cap (beginning of the 19th century) which was made possible with the discovery of fulminates as impact sensitive initiating materials.

Modern initiation systems for all sorts of applications (handguns, large caliber artillery cannons, bombs, mining charges, etc.) are practically immune to environmental conditions and rely on the use of pyrotechnical mixtures and primary explosives. The two existing types of initiators are the previously mentioned detonator (shock wave output) and the igniter (flame output). The latter is usually used to initiate propellant charges or fireworks, for example.[4] The thinning of the primary explosive with additives in the priming mix prevents the formation of an, in this case unwanted, shock wave, similar to the use of secondary explosives in modern gun propellants (see above). Figure 1.5 gives an overview of the commonly used detonator types and their schematic setup. As already mentioned, primary explosives are able to undergo a DDT after a SII notably in the form of direct heat or heat-generating stimuli like impact or friction (or a combination of both), thus they operate on the same basic principles as the historical initiators.

The non-electric flame initiators (figure 1.5 A) are the cheapest type of detonators in which the primer (mostly a pyrotechnic mixture) is initiated by the flame of a burning safety fuse.[15] A more advanced version is the class of hot-wire initiators in which a bridgewire embedded into a pyrotechnical mixture (figure 1.5 B) or a primary explosive (figure 1.5 C) is heated up by an electrical current to produce the necessary energy for ignition.[15] Blasting caps for mining and demolition usually use this type of initiation. Another non-electric initiator is the stab detonator (figure 1.5 D) like the M55,[15] basically a more advanced form of the percussion cap, which uses a combination of impact and friction. A firing pin pierces the closing cap of the detonator and accelerates into the priming mix (e.g. NOL-130) upon activation. Thermal energy is released in front of the pin as a result of compressing

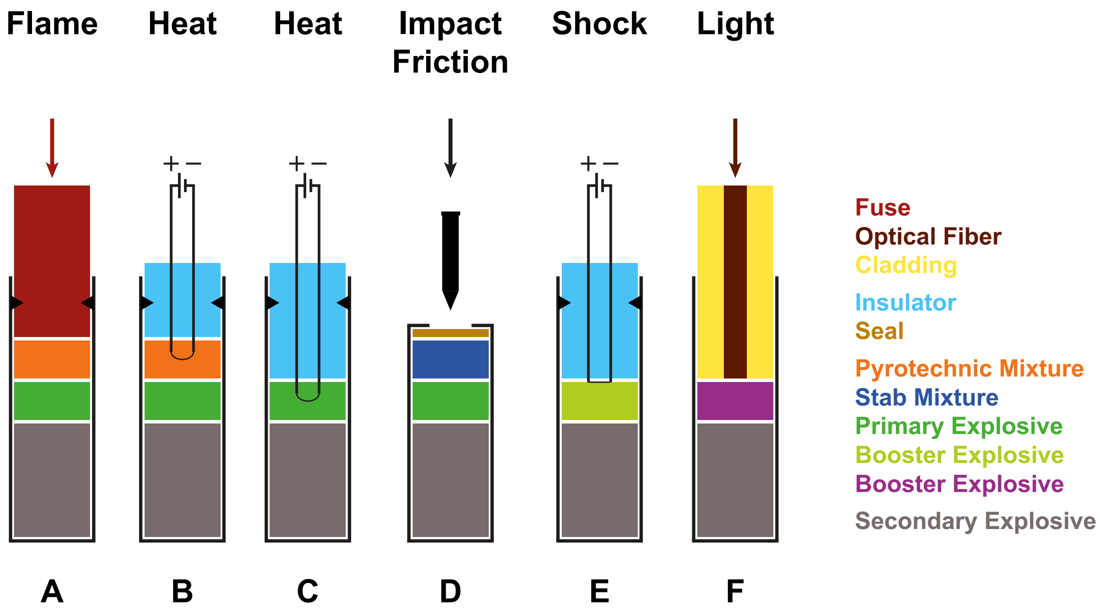


Figure 1.5: Schematic set-up of the most common detonator types: A) flame; B) electric match; C) hot-wire; D) stab; E) exploding bridgewire; F) laser.

the mix and to the side as a result of the generated friction. This type of detonator is widely used for military applications, including anti-tank warheads and landmines like the M14 (see figure 1.6 for a schematic cutaway view), in which kinetic energy is eventually transferred to the firing pin and thus used for the initiation. The rimfire and centerfire percussion primers used for small-caliber cartridges function comparably to stab detonators except for not being pierced by a pin but instead hit by a hammer and only produce a flame output.[15] The two already mentioned priming compositions SINOXID and SINTOX are commonly used for these kinds of initiators. Also in use are exploding bridgewire detonators (EBWs, figure 1.5 E),[15] which are mainly used as initiators in nuclear devices,[41] owing to their precise and consistent function times of less than 1 µs (hot-wires typically measure at around 1000 µs).[42] The utilized gold or gold/platinum alloy wires are not used to heat up a primer but to actually physically explode themselves. This is achieved by a rapid heating of the wire by transmission of a high current (supplied by a low-inductance, high-voltage capacitor) leading to melting and subsequent vaporization. Due to the rapidity of the heating and the wire's own mass inertia the metal is prevented from moving away. Following the vaporization, the resistance increases abruptly which in turn leads to a breakdown of the current, finally allowing the super-heated particles to explosively expand and generate a shock wave in the process. Although EBWs could in theory directly use a secondary explosive as a result of this shock wave, only PETN at 50 % of its crystal density can be initiated due to the limited energy output. A more modern approach is the use of pulsed lasers as SII (figure 1.5 F) which rely on special primary and booster explosives susceptible

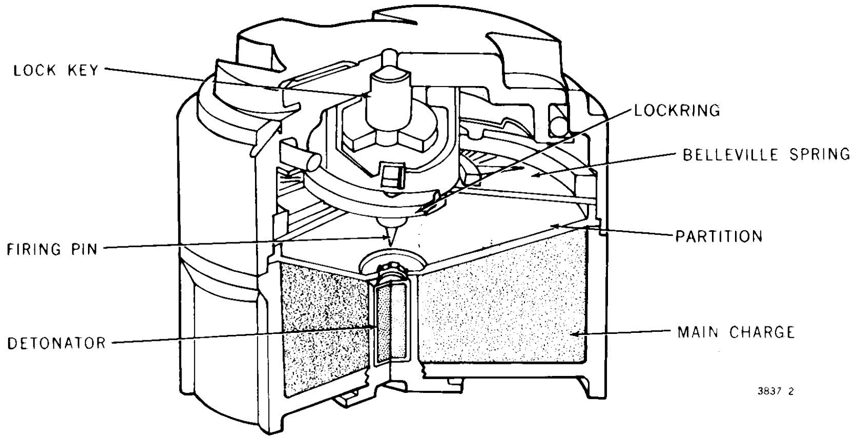


Figure 1.6: Schematic cutaway view of the U.S. M14 landmine,[47] utilizing a stab detonator as initiator. Initially employed during the Korean and Vietnam War it is currently still utilized in several countries in Africa, Middle East and Mainland Southeast Asia.

to the thermal heat of laser irradiation.[35,36,43–45] These are usually energetic complexes like the above mentioned BNCP, but PETN can be used as well.[43] A recent thesis from our group was solely dedicated to this type of primary explosives.[46] In comparison to the flame and electrical initiators these are even more immune to environmental hazards, like electrostatic discharge, which could lead to malfunctions or premature firing. They can likewise utilize less impact and friction sensitive primary explosives which further enhances the safety, especially during the manufacturing process of the compounds and the detonators.

1.4 Concept and Goal

As previously mentioned, although a wide range of tetrazole derivatives and their heavy metal salts have been investigated as potential lead azide replacements over the past century, only few investigations concerning the use of triazoles (1,2,4 and 1,2,3) as primary explosives could be found.[48–53] Although 1,2,4-triazole itself is less energetic than tetrazole ($\Delta_\mathrm{f}H^\circ{}_\mathrm{(s)} = 109\,\mathrm{kJ\,mol^{-1}}$ versus $\Delta_\mathrm{f}H^\circ{}_\mathrm{(s)} = 237\,\mathrm{kJ\,mol^{-1}}$),[54,55] it exhibits a higher thermal stability and two carbon atoms instead of one, allowing a wider range of substitution with various energetic groups. An approach to increase the enthalpy of formation and bring some desired instability into the molecule could be the utilization of the azido group on one of the carbon atoms. This general idea was previously investigated in the form of a master's thesis with 3-azido-1*H*-1,2,4-triazole and 3,5-diazido-1*H*-1,2,4-triazole.[56] Unfortunately, both compounds show rather low thermal stabilities (around 130 °C), due to a missing proper second substituent or an azide being the second one. The idea was now to find more suitable energetic groups for the second carbon atom and to investigate the effects on both the thermal stability and the tendency of the compounds to either be primary explosives by themselves or to form primary explosives with suitable cations.

The most suitable cation to test both the capability for salt formation and the energetic properties of the neutral compounds was deemed to be silver, owing to the usually low solubility of azole silver salts in water and thus their facile preparation. Silver salts additionally feature the best energetic performance of the metal cations,[12] and are therefore well suited for identification purposes. This means that if the silver salt is not a proper primary explosive and incapable of a DDT then the other salts will most probably also fail. Unfortunately, silver salts bear some problems, making them rather unfeasible for commercial applications, including oftentimes a sensitivity towards light, high costs and the toxicity of silver for microorganisms and aquatic life.[57,58] More useful cations include the alkali metals potassium and cesium or transition metals like copper(I), copper(II) and zinc. Potassium, for example, is utilized in KDNP and copper(I) in DBX-1. However, it should be mentioned that copper(II) is also toxic for microorganisms,[59] but to a lower degree than silver and is therefore not yet deemed undesired.[60] Other heavy metals like cadmium, mercury and lead, which are of course no longer desirable but were utilized in the past, can be of comparative value concerning the thermal stability and energetic performance and are thus of academical interest. Manganese, iron, cobalt and nickel are also possible cations but usually tend to form highly hydrated compounds, unfortunately, resulting in a decrease of performance.

Suitable simple test methods to identify primary explosives are, of course, heating and burning. Due to the capability to undergo a DDT, a true primary explosive detonates when slowly heated, for example on a metal spatula or plate with a lighter or bunsen burner from below without any flame contact, while secondary explosives simple deflagrate or burn. Deflagration thus indicates an extremely slow DDT (confinement needed) or none at all. More potent primary explosives like lead and silver azide with a very fast DDT also detonate when rapidly heated or when directly burned, even in the smallest quantities. The hot-needle test, in which the material is touched with a preheated needle, is thus well suited to identify the true performance of a primary explosive concerning its DDT.[61] Contrary to slow heating it offers benefits like the prevention of preliminary removal of crystal water, moisture and other contaminants which can usually negatively effect the DDT of a substance as a result of the rapid punctual heating. Primary explosives which detonate with this test method are thus much more suitable for practical applications. It should be noted that some highly sensitive compounds like tetrazene are no true primary explosives by themselves (only deflagration upon unconfined heating), but serve as sensitizers in priming mixtures for stab and percussion initiators.

The general goal of this investigation was thus the preparation of azido-1,2,4-triazole derivatives with various energetic groups as the second substituent, in order to identify any true primary explosives among them. If a respective silver salt passed the basic tests, then additional salts with other cations were prepared and similarly tested. The final test was the capability to initiate a common secondary explosive like RDX, which was exclusively tested with potassium or cesium salts and not with silver salts due to their more practical potential use.

Additionally, other selected azole based compounds and their salts were also investigated in the same fashion, including 1,2,3-triazoles, nitrimino-1,2,4-triazoles and tetrazoles.

Finally, for potential practical applications, the prepared compounds should ideally meet the following, general requirements:[62]

- Capable of initiating a secondary explosive
- Environmentally acceptable metals (K, Cs, Zn, Fe, Bi, etc.)
- Decomposition temperature (T_d): $\geq 180\,°\mathrm{C}$ (at the very least $\geq 150\,°\mathrm{C}$)
- Impact sensitivity (IS): 1 to 5 J
- Friction sensitivity (FS): 5 to 15 N
- Minimum number of synthetic steps

Publications Most of the following chapters have been published as articles, or as parts thereof, in peer-reviewed scientific journals (*Central European Journal of Energetic Materials*; *Chemistry – A European Journal*; *Crystals*; *European Journal of Inorganic Chemistry*; *Propellants, Explosives, Pyrotechnics*; *Zeitschrift für Anorganische und Allgemeine Chemie*) and as poster contributions at the annual international seminar *New Trends in Research of Energetic Materials* (2012–2015). The published articles were slightly modified to properly fit together as a thesis, including new introductions, additional minor improvements and removal of the results of co-authors.

1.5 General Methods and Characterization

Caution! *Most compounds prepared herein are energetic compounds sensitive to impact, friction and electrostatic discharge. Although there were rarely any problems in handling the compounds, proper protective measures (ear protection, Kevlar® gloves, face shield, body armor and earthed equipment) should be used, especially when working with oftentimes highly sensitive silver salts.*

Analytical Methods

NMR spectra were recorded using the spectrometers JEOL Eclipse 270, JEOL Eclipse 400, JEOL ECX 400 and Bruker Avance III 400. The measurements were conducted in regular glass NMR tubes (⌀ 5 mm) and, if not stated otherwise, at 25 °C. Tetramethylsilane (^{1}H, ^{13}C) and nitromethane ($^{14/15}$N) were used as external standards. As additional internal standard the reference values of the partially deuterated solvent impurity (^{1}H) and the fully deuterated solvent (^{13}C) were used.[63]

Infrared (IR) spectra were recorded on a PerkinElmer BX FT IR spectrometer equipped with a Smiths DuraSamplIR II diamond ATR unit with pure samples. Transmittance values are qualitatively described as “very strong” (vs), “strong” (s), “medium” (m), “weak” (w) and “very weak” (vw).

Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser operating at 1064 nm and a reflection angle of 180° in open glass tubes (⌀ 5 mm). The intensities are reported as percentages of the most intense peak and are given in parentheses.

Low resolution mass spectra were recorded on a JEOL MStation JMS-700, with 4-nitrobenzyl alcohol as matrix for FAB measurements.

Determination of the carbon, hydrogen and nitrogen contents was carried out by combustion analysis using an Elementar Vario EL. The determined nitrogen values are often lower than the calculated ones, which is common for nitrogen-rich compounds and cannot be avoided. Highly energetic compounds, especially primary explosives, also often tend to give generally unsatisfactory measurements due to their explosive behavior.

Differential scanning calorimetry was conducted with a Linseis DSC-PT10 in closed aluminum pans, equipped with a hole (⌀ 0.1 mm) for gas release, and a heating rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$. Differential thermal analysis was conducted with an OZM Research DTA 552-Ex in open glass tubes (diameter 4 mm, length about 47 mm) at a heating rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$. The reported temperatures are not the extrapolated onsets (second derivation of the curve) but the beginning point of the signal for better comparison due to mostly broad signals. Melting points were checked with a Büchi Melting Point B-540 in open glass capillaries. Isoperibolic long term measurements were conducted in open glass vessels with a Systag Flexy TSC equipped with a Radex V5 measuring cell.

Crystal structures were determined by single crystal X-ray diffraction on an Oxford Diffraction Xcalibur 3 diffractometer with a Sapphire CCD detector, four circle kappa platform, Enhance molybdenum K_{α} radiation source ($\lambda = 71.073$ pm) and Oxford Cryosystems Cryostream cooling unit. Data collection and reduction were performed with CrysAlisPro.[64] The structures were solved with SIR97,[65] or SHELXS-97,[66] refined with SHELXL-97,[66] or SHELXL-2013,[67] and finally checked with PLATON,[68] all integrated into the WinGX software suite.[69] The finalized CIF files were checked with checkCIF,[70] and deposited at the Cambridge Crystallographic Data Centre.[71] Intra- and intermolecular contacts were analyzed with Mercury.[72] The illustrations of molecular structures were drawn with ORTEP-3.[73]

Sensitivities

Sensitivities to impact (IS) and friction (FS) were determined according to BAM standards,[74] using a BAM drop hammer and a BAM friction apparatus.[75–80] The compounds were classified in compliance with UN guidelines.[81] Impact: insensitive $> 40\,\mathrm{J}$, less sensitive $\geq 35\,\mathrm{J}$, sensitive $\geq 4\,\mathrm{J}$, very sensitive $\leq 3\,\mathrm{J}$; Friction: insensitive $> 360\,\mathrm{N}$, less sensitive $= 360\,\mathrm{N}$, sensitive $< 360\,\mathrm{N}$ and $> 80\,\mathrm{N}$, very sensitive $\leq 80\,\mathrm{N}$, extremely sensitive $\leq 10\,\mathrm{N}$. Sensitivities to electrostatic discharge (ESD) were determined with an OZM Research ESD 2010 EN. The compounds were sieved to determine the grain size ($< 100\,\mu\mathrm{m}$, 100 to $500\,\mu\mathrm{m}$, $> 500\,\mu\mathrm{m}$).

Calculated Heats of Formation

Nitrogen-rich highly energetic compounds tend to burn incompletely in bomb calorimetric measurements due to the trend of explosion. Oftentimes wrong enthalpies of combustion ($\Delta_\mathrm{c}H$) and finally wrong enthalpies of formation ($\Delta_\mathrm{f}H^\circ$) are obtained. Therefore the enthalpies and energies of formation were calculated at the CBS-4M level of theory as implemented in Gaussian 09,[82–84] using the atomization energy method and utilizing experimental data.[85–89] Gas phase enthalpies were transformed to solid state enthalpies by using Trouton's rule for neutral compounds,[90,91] and Jenkin's method for ionic compounds.[92–94] The complete method is extensively described in the literature.[3] The molar energy ΔU and enthalpy of formation ΔH of a compound $\mathrm{C}_a\mathrm{H}_b\mathrm{N}_c\mathrm{O}_d$ are connected according to

$$\Delta H = \Delta U + \Delta nRT, \tag{1.1}$$

in which Δn is the change of moles of the gaseous components in the equation of formation,

$$a\,\mathrm{C} + \frac{b}{2}\,\mathrm{H}_2 + \frac{c}{2}\,\mathrm{N}_2 + \frac{d}{2}\,\mathrm{O}_2 \longrightarrow \mathrm{C}_a\mathrm{H}_b\mathrm{N}_c\mathrm{O}_d. \tag{1.2}$$

5-Azido-3-nitro-1*H*-1,2,4-triazole

D. Izsák, T. M. Klapötke
Crystals **2012**, *2*, 294–305

D. Izsák, T. M. Klapötke, R. Scharf, J. Stierstorfer
Z. Anorg. Allg. Chem. **2013**, *639*, 1746–1755

2.1 Introduction

One of the oldest yet to this day still one of the most frequently employed energetic building blocks is the nitro group.[9] Well known examples of primary explosives with one or several nitro groups are lead styphnate, KDNP, and several salts of 5-nitro-2*H*-tetrazole,[2,4] including DBX-1.

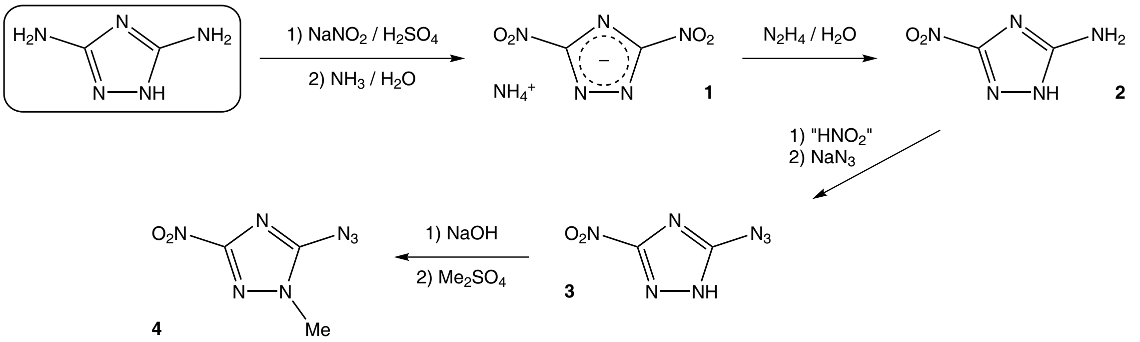
In the effort to develop a compound with a higher performance than 3-azido-1*H*-1,2,4-triazole (**50**) but lower sensitivity than 3,5-diazido-1*H*-1,2,4-triazole,[56] substituting a nitro group for the proton or the second azide, respectively, could create an ideal candidate. Although the resulting title compound 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) has already been reported no later than 1974,[95] no data on its preparation or characterization could be found. Even though two publications mention its potential use as an energetic material,[53,96] no characterization or data was provided. While most of the already reported azido-1,2,4-triazoles are either difficult to prepare, or have low reaction yields, **3** further caught the eye due to the facile preparation of the possible starting material 5-amino-3-nitro-1*H*-1,2,4-triazole (**2**).[97] The latter was developed as a potential RDX replacement and exhibits a very good thermal stability (up to 220 °C).

Therefore, the goal of this study has been the synthesis and comprehensive characterization of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**), including the formation of the corresponding less toxic metal as well as nitrogen-rich salts and ultimately the investigation of their potential use as eco-friendly new primary and secondary explosives.

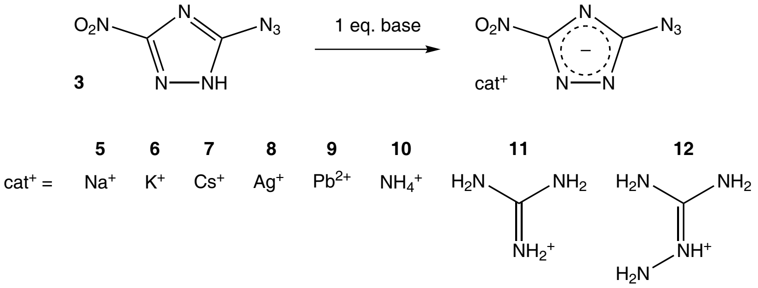
2.2 Results and Discussion

2.2.1 Syntheses

Starting with commercially available 3,5-diamino-1*H*-1,2,4-triazole, which was diazotated with a tenfold excess of sodium nitrite in dilute sulfuric acid, leading to the substitution



Scheme 2.1: Synthesis of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) and its derivative 5-azido-1-methyl-3-nitro-1,2,4-triazole (**4**) from commercially available 3,5-diamino-1*H*-1,2,4-triazole.



Scheme 2.2: Synthesis of the energetic salts **5**–**12** of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**).

of both amino groups with nitro groups. The highly hygroscopic 3,5-dinitro-1*H*-1,2,4-triazole could be isolated as its ammonium salt (**1**) upon treatment with aqueous ammonia solution.[98] Refluxing with five equivalents hydrazine monohydrate reduced selectively one nitro group and furnished 5-amino-3-nitro-1*H*-1,2,4-triazole (**2**).[98] Diazotation of **2** with sodium nitrite in 25 % sulfuric acid and subsequent reaction with sodium azide yielded 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**). Further reaction with dimethyl sulfate in aqueous sodium hydroxide solution yielded the methyl derivative **4**.

The alkali metal salts with sodium (**5**), potassium (**6**) and cesium (**7**), as well as the nitrogen-rich salts with ammonium (**10**), guanidinium (**11**) and aminoguanidinium (**12**) were prepared in ethanolic solution using **3** and the corresponding carbonates, hydrogen carbonates, or free bases and subsequent removal of the solvent under reduced pressure. The silver salt **8** was prepared by the reaction of **3** with silver nitrate in water. The lead salt **9** was prepared by the reaction of lead nitrate with in situ prepared **5** in water. A copper(I) salt was also attempted but no clear-cut product could be obtained.

2.2.2 Crystal Structure Analysis

5-Azido-3-nitro-1*H*-1,2,4-triazole (**3**) crystallized in the orthorhombic space group *Pnma* with four molecules in the unit cell. The calculated density at 173 K is 1.774 $\mathrm{g\,cm^{-3}}$, which

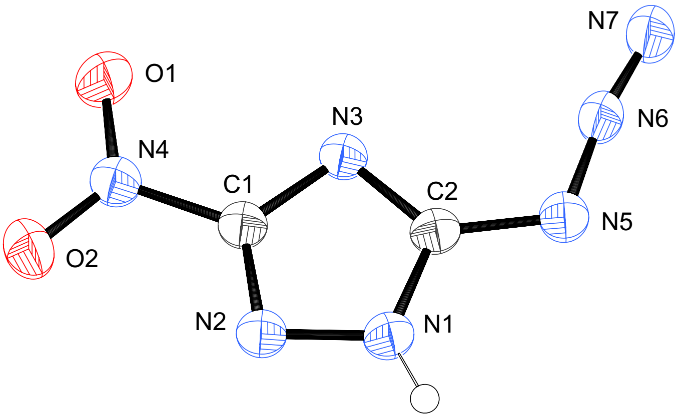


Figure 2.1: Molecular structure of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**). Thermal ellipsoids at 50 % probability.

is lower than that of the reactant **2** (1.841 g cm^{-3}) at room temperature.[99] The asymmetric unit consists of one complete molecule (figure 2.1). The structure of **3** is similar to other disubstituted 1,2,4-triazoles with the C-N and N-N bonds of the ring being between formal single and double bonds.[100] N1–C2 (1.345(2) Å), N3–C1 (1.350(2) Å) and N1–N2 (1.356(2) Å) exhibit a higher single bond character, while N2–C1 (1.314(2) Å) and N3–C2 (1.327(2) Å) exhibit a higher double bond character. This also affects the angles within the ring, with only N2–C1–N3 (118.5(1)°) being close to sp^2 hybridization (120°). N1–C2–N3 and N2–N1–C2 are both around 110°, while C1–N3–C2 and N1–N2–C1 are both around 100°. The N4–C1 bond connecting the nitro group to the ring is the longest bond with 1.452(2) Å and therefore almost a true single bond. The O-N bonds are similar (O1–N4: 1.227(1) Å; O2–N4: 1.228(1) Å) with a high double bond character.[100] The O1–N4–O2 angle is 124.9(2)°, which is common for aromatic nitro groups.[101] The N5–C2 bond shows a high single bond character with 1.383(2) Å. The constitution of the azido group is similar to other covalent azides, for example 5-azido-1*H*-tetrazole.[102] The N5–N6 bond (1.256(2) Å) is in the range of a N-N double bond and N6–N7 (1.124(2) Å) is close to a formal N-N triple bond.[100] The N5–N6–N7 angle (170.4(2)°) deviates as expected from 180°, which can be explained by hyperconjugation effects.[103] The torsion angles N2–C1–N4–O1 and N1–C2–N5–N6 are both 180.0(2)°, showing a complete planarity of the molecule. The structure of **3** in the crystalline state is characterized by infinite chains of alternating molecules along the *a* axis in the *a*-*c* plane, connected by bifurcated hydrogen bonds (figure 2.2 and table 2.1). The N1–H71$\cdots$O1$^{\text{i}}$ contact is less directed with an angle of 135(2)° than the N1–H71$\cdots$N3$^{\text{i}}$ contact with 153(2)°, and both are fairly weak with practically identical donor acceptor distances (N1$\cdots$O1$^{\text{i}}$: 3.013(2) Å; N1$\cdots$N3$^{\text{i}}$: 3.015(2) Å) just slightly under the sum of the van der Waals radii ($\sum r_{\text{w}}(\text{N,O}) = 3.07$ Å, $\sum r_{\text{w}}(\text{N,N}) = 3.10$ Å).[104] The hydrogen bonds are therefore mostly of an electrostatic nature,[105] forming a five-membered

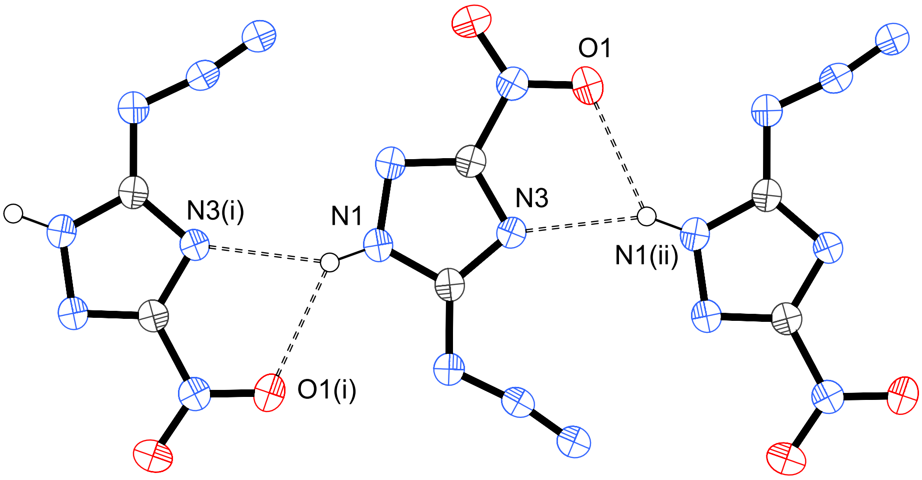


Figure 2.2: Hydrogen bonding scheme of 5-azido-3-nitro-1H-1,2,4-triazole (**3**), illustrating the infinite chains along the a axis in the a-c plane. Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $x-0.5, -y+0.5, -z+0.5$; (ii) $x+0.5, -y+0.5, -z+0.5$.

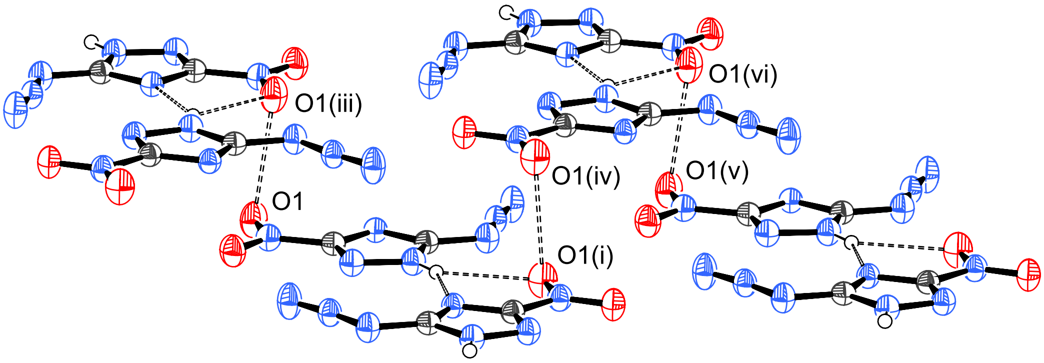


Figure 2.3: Packing scheme of 5-azido-3-nitro-1H-1,2,4-triazole (**3**), showing the short contacts connecting the layers along the b axis. Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $x-0.5, -y+0.5, -z+0.5$; (iii) $-x+1, y+0.5, -z$; (iv) $-x+0.5, -y+1, z+0.5$; (v) $x, y, z+1$; (vi) $-x+1, y+0.5, -z+1$.

ring. The chains build up a layer structure in which one layer consists of identical parallel chains with no interaction between them. The second layer consists of anti-parallel chains, in relation to the first layer, with the molecules being above the gaps of the first layer. The layers are thus connected by an O-O short contact $\mathrm{O1}\cdots\mathrm{O1}^{\mathrm{iii}}$, with the atoms being almost directly above each other along the b axis. The distance of 2.9633(4) Å is only slightly shorter than the sum of the van der Waals radii ($\sum r_\mathrm{w}(\mathrm{O,O}) = 3.04$ Å),[104] indicating a weak interaction. The packing of the molecules is depicted in figure 2.3.

5-Azido-1-methyl-3-nitro-1,2,4-triazole (**4**) crystallized in the monoclinic space group $P2_1/m$ with two molecules in the unit cell. The asymmetric unit consist of one molecule and is depicted in figure 2.4, together with the atom labeling scheme. The structure of the ring system is identical to the parent compound **3**. The N1–C3 bond is a true single bond

Table 2.1: Hydrogen bonds present in 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**).

D–H···A	*d*(D–H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠(D–H···A) / °
N1–H71···O1^{i}	0.85(3)	2.36(2)	3.013(2)	135(2)
N1–H71···N3^{i}	0.85(3)	2.24(3)	3.015(2)	153(2)

Symmetry code: (i) $x - 0.5, -y + 0.5, -z + 0.5$.

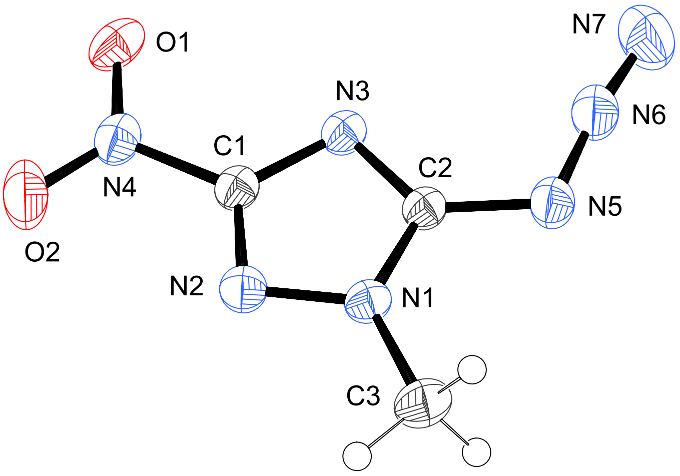


Figure 2.4: Molecular structure of 5-azido-1-methyl-3-nitro-1,2,4-triazole (**4**). Thermal ellipsoids at 50 % probability.

with 1.463(4) Å. A discussion of hydrogen bonds is omitted due to the hydrogen atoms being calculated as an idealized methyl group (HFIX 33), although the crystal packing shows the possibility of a very weak electrostatic interaction between C3 and N3^{ii} (figure 2.5). The structure is again comprised of parallel chains along the *a* axis forming a layer structure, whereby the alternating layers feature anti-parallel chains, quite similar to **3**. But contrary to **3** the molecules are not above the gaps of the surrounding layers, but rather directly above each other. This is the result of four O-C and N-N short contacts (O1–C1^{i}: 3.0351(9) Å; N3–N4^{i}: 3.0448(8) Å), all of which are well below the sum of the van der Waals radii ($\sum r_{\mathrm{w}}$(C,O) = 3.22 Å).[104]

Potassium 5-azido-3-nitro-1,2,4-triazolate (**6**) crystallized in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The calculated density at 173 K is 1.933 g cm^{-3} and interestingly only slightly higher than that reported for potassium 5-azidotetrazolate (1.913 g cm^{-3}).[29] The asymmetric unit, depicted in figure 2.6, consist of one ion pair. The deprotonation of the ring leads to a fully delocalized π system, with C-N bond lengths between 1.327(2) Å (N2–C1) and 1.343(2) Å (N1–C2 and N3–C1), and a N1–N2 bond length of 1.374(2) Å. The angles of the ring are more symmetrical than in **3**, with N1–C2–N3 and N2–C1–N3 both being around 120°, close to an sp^2 hybridization. N1–N2–C1, N2–N1–C2 and C1–N3–C2 are all round 100°, with the former two slightly higher and the latter

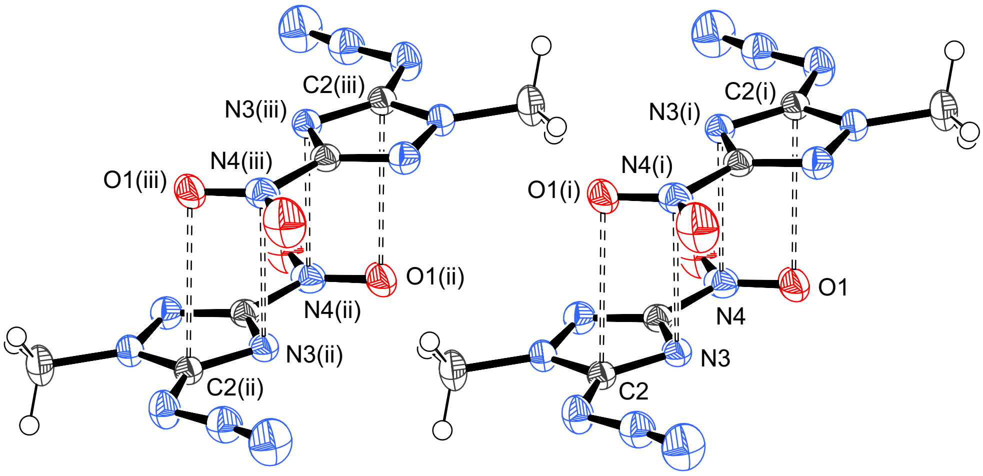


Figure 2.5: Packing scheme of 5-azido-1-methyl-3-nitro-1,2,4-triazole (**4**), showing the short contacts connecting the layers along the b axis. Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x+2, y-0.5, -z$; (ii) $x-1, y, z$; (iii) $-x+1, y-0.5, -z$.

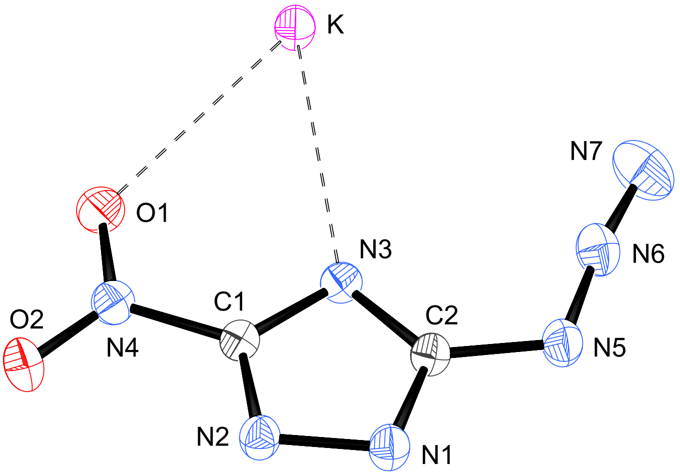


Figure 2.6: Molecular structure of potassium 5-azido-3-nitro-1,2,4-triazolate (**6**). Thermal ellipsoids at 50 % probability.

slightly lower. While the N4–C1 bond between the ring and the nitro group is shortened to 1.441(2) Å, the N5–C2 bond connecting the ring with the azide grew to 1.410(2) Å, with both still showing a high single bond character. The bond lengths and angles of the azido and the nitro groups are nearly identical to those of **3**. While the N2–C1–N4–O1 torsion angle shows a nearly complete planarity between the ring and the nitro group (179.0(1)°) the azide is slightly bent out of ring plane with an N1–C2–N5–N6 angle of −174.9(1)°. The potassium cation lies slightly above the molecule plane with torsion angles around 20° for N3···K···O1–N4 and O1···K···N3–C1. The coordination of the potassium cation is ninefold and resembles a distorted singly capped tetragonal prism. The distances are between 2.847(1) Å (K···O1) and 3.084(1) Å (K···N2$^{\text{iv}}$), with the contacts within the asymmetric unit being 2.847(1) Å (K···O1) and 2.902(1) Å (K···N3).

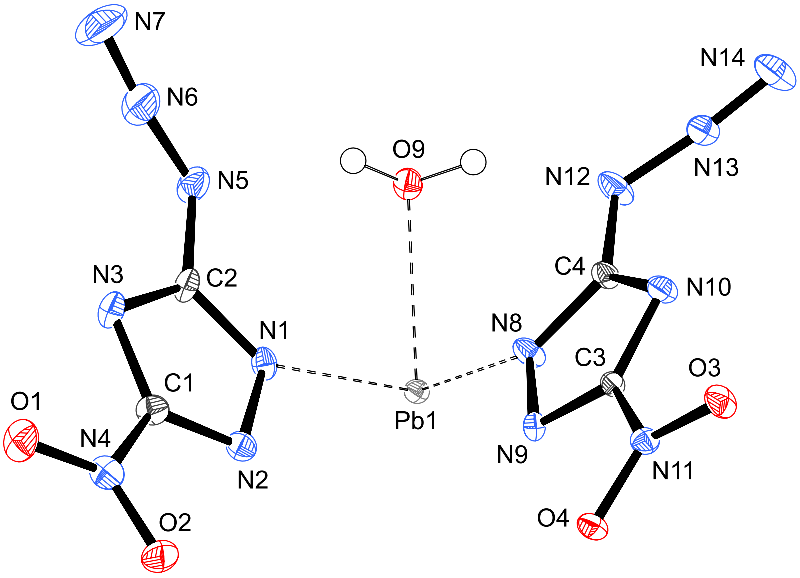


Figure 2.7: One of the two independent molecular units of lead bis(5-azido-3-nitro-1,2,4-triazolate) monohydrate (**9**). Thermal ellipsoids at 50 % probability.

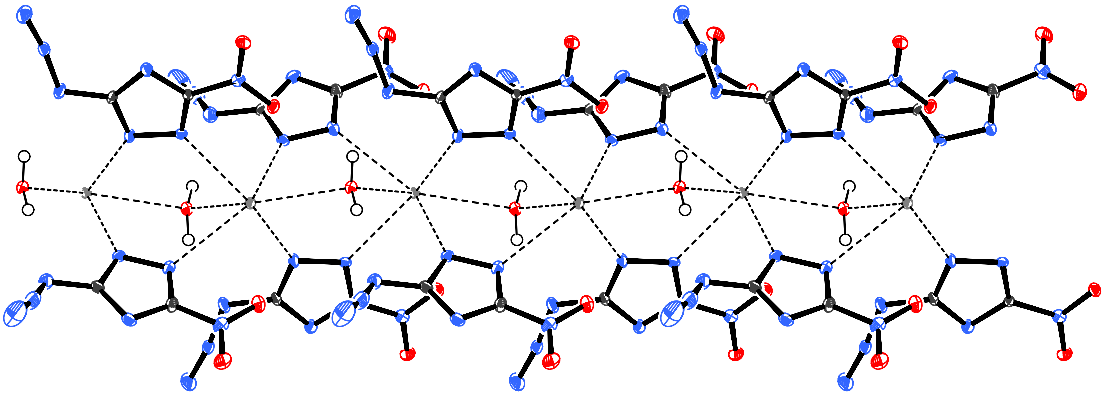


Figure 2.8: View on the chains present in the crystal structure of lead bis(5-azido-3-nitro-1,2,4-triazolate) monohydrate (**9**). Thermal ellipsoids at 50 % probability.

Lead bis(5-azido-3-nitro-1,2,4-triazolate) monohydrate (**9**) crystallized in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell. The asymmetric unit consists of two independent molecular units, one of which is depicted in figure 2.7. The structure is made up by infinite chains along the b axis. One such chain is depicted in figure 2.8. The chains are parallel along the b axis and stacked along the c axis. While there are only weak van der Waals interactions to the sides, a weak and mostly electrostatic hydrogen bond (O9–H91$\cdots$N10$^{\text{ii}}$) is present along the stacking (see table 2.2).

2.2.3 NMR Spectroscopy

Compounds **3**–**7** and **10**–**12** were analyzed by ^{1}H, ^{13}C and ^{14}N NMR spectroscopy in DMSO-d_6, with **3**, **4** and **6** additionally by ^{15}N NMR spectroscopy. In the ^{1}H NMR spectrum, the

Table 2.2: Hydrogen bonds present in lead bis(5-azido-3-nitro-1,2,4-triazolate) monohydrate (**9**).

D–H···A	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	∠(D–H···A) / °
O9–H91···N5	0.90(3)	2.00(4)	2.773(6)	143(4)
O9–H92···N12	0.89(6)	2.01(6)	2.823(7)	152(5)
O9–H92···O4^{i}	0.89(6)	2.54(6)	3.094(5)	121(4)
O9–H91···N10^{ii}	0.90(3)	2.63(6)	3.179(5)	121(4)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+1, -z$.

highly acidic nitrogen bonded proton in **3** is found at 9.73 ppm as a very broad signal. In less basic acetonitrile-d_3 it is located at 10.74 ppm as a narrower, but still broad, signal. The precursor **2** in contrast shows two sharp singlets at 13.14 (ring proton) and 6.80 ppm (NH_2). In **4** the methyl proton shifts are found at 3.74 ppm. While the ammonium cation proton resonances in **10** are located at 7.14 ppm, the three equivalent amine groups of the guanidinium cation of **11** show a sharp signal at 6.92 ppm. The aminoguanidinium cation of **12** shows four signals, in accordance to the four different types of protons, located at 8.58 (NH), 7.27 ($C-NH_2$), 6.77 ($C-NH_2$) and 4.69 ppm ($N-NH_2$). In all ^{13}C NMR spectra both triazole carbon atoms are observed. For the neutral compounds C1 can be observed at 160.3 (**3**) and 158.7 ppm (**4**), and C2 at 151.8 (**3**) and 150.3 ppm (**4**). Compound **4** additionally shows the resonance of the methyl group C3 at 35.4 ppm. The deprotonation of the ring greatly affects the shifts of both carbon atoms, leading to a down field shift for C1 and a high field shift for C2. The signals of C1 are thus located between 163.6 and 163.9 ppm, while the C2 signals are between 155.7 and 156.2 ppm. The two guanidinium salts (**11** and **12**) show the signal of the cation at 157.9 and 158.8 ppm, respectively. The ^{14}N NMR spectrum of all compounds shows the resonance of the nitro group and the azide beta nitrogen atom. While the former is at −22 ppm in **3** and at −23 ppm in **4**, deprotonation results in a down field shift with the signal now being between −12 and −15 ppm. The signal of the azide is at −141 and −142 ppm for **3** and **4**, respectively, and again down field shifted in the anionic compounds, being between −133 and −134 ppm. Compound **10** additionally shows the shift of the ammonium nitrogen atom at −354 ppm. The ^{15}N NMR spectra of **3**, **4** and **6** are illustrated in figure 2.9. In the case of **3** and **4** also the proton de-coupled $^{15}N\{^1H\}$ NMR spectra were recorded. The assignments were based on comparison with theoretical calculations (MPW1PW91/aug-cc-pVDZ). In the case of **3** seven definite resonances can be observed at shifts of −20.9 (N4), −91.6 (N2), −137.0 (N7), −139.9 (N6), −154.0 (N3), −172.7 (N1) and −285.9 ppm (N5), with N2 not being visible in the $^{15}N\{^1H\}$ NMR spectrum. A N-H coupling of N1 and N2 is not observable due to the high acidity and therefore fast proton exchange in DMSO. Compound **4** shows

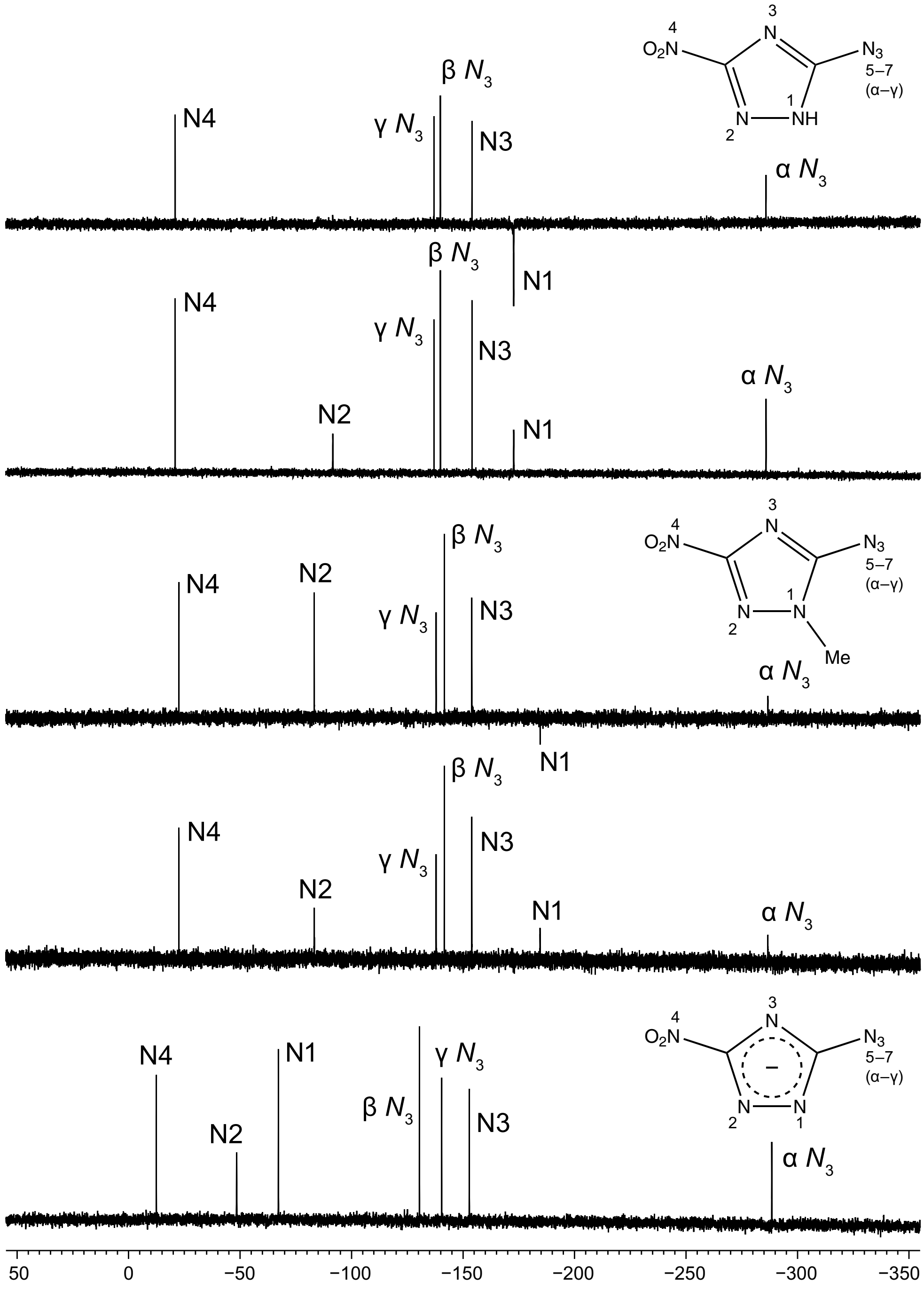


Figure 2.9: ^{15}N and $^{15}N\{^1H\}$ NMR spectra of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**), 5-azido-1-methyl-3-nitro-1,2,4-triazole (**4**) and potassium 5-azido-3-nitro-1,2,4-triazolate (**6**) in DMSO-d_6 at room temperature.

signals at −22.6 (N4), −83.3 (N2, q), −137.9 (N7), −141.6 (N6), −153.9 (N3), −184.6 (N1, q) and −288.7 ppm (N5). The methylation at N1 leads to a high field shift for N1 (Δ(N1) = −11.9 ppm) and a similar down field shift for N2 (Δ(N2) = 8.3 ppm), while the shifts of the other nitrogen atoms are only marginally affected. Both cores couple with the hydrogen atoms of the methyl group, leading to a ^2J coupling of N1 with a coupling constant of $^2J_{\mathrm{NH}} = 2.11\,\mathrm{Hz}$ and a ^3J coupling of N2 with a coupling constant of $^3J_{\mathrm{NH}} = 2.03\,\mathrm{Hz}$. The deprotonation in **6** leads to a large down field shift of N1 to −67.2 ppm (Δ(N1) = 105.5 ppm), a smaller of N2 to −48.5 ppm (Δ(N2) = 43.1 ppm), and also N4 is shifted to −12.4 ppm (Δ(N4) = 8.5 ppm). This is in accordance to 5,5′-bis(3-nitro-1*H*-1,2,4-triazole) and its dianion.[106] Interestingly, N6 is also affected and shifted to −130.4 ppm (Δ(N6) = 9.5 ppm). The other shifts are virtually the same as in **3** and **4**, leading to the remaining signals being observable at −140.4 (N7), −152.8 (N3) and −288.5 ppm (N5).

2.2.4 Thermal Stabilities

Differential scanning calorimetry measurements were performed in order to determine the thermal behavior of the synthesized compounds. The decomposition temperatures of the investigated compounds range from 130 °C (**9**) up to 185 °C (**7**). The neutral compound **3** as well as the methyl derivative **4** both show distinct melting points (110 and 115 °C, respectively). The ammonium (**10**) and aminoguanidinium (**12**) salts melt under decomposition (139 and 138 °C, respectively). Although the sodium salt **5** has a difference of 28 °C between loss of crystal water and decomposition it could not be dehydrated completely, as evidenced by IR spectroscopy and DSC. The lead salt **9** also could not be dehydrated, as there is no sign of water loss before decomposition. The most stable compounds are the salts with guanidinium (**11**) and cesium (**7**), showing decomposition at 160 and 185 °C, respectively. Compound **3** itself and the potassium salt **6** show similar decomposition temperatures of 149 and 152 °C, respectively. Furthermore both **3** and **6** are thermally stable for at least 48 hours at 75 °C in an open glass vessel, as evidenced by isoperibolic long term measurements which resulted in neither any signals, nor a weight loss or color change of the samples after the measurement. Usually the deprotonation of nitroazoles raises the stability of the system by overcompensation of the electron-withdrawing effect of the nitro group (besides a higher lattice energy in the crystalline state due to the ionic nature). However, in the investigated system it mostly decreases the thermal stability, i.e. the benefits of deprotonation can hardly compensate for the negative effect of the higher electron density of the system. 5-Nitramino-3-nitro-1*H*-1,2,4-triazole, for example, is reported with a decomposition temperature of 135 °C, while the corresponding ammonium salt is stable until 205 °C and the guanidinium salt until 220 °C, with the bis(guanidinium) salt decomposing at 225 °C.[107] Also 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole is reported with a rather low decomposition temperature (143 °C), while all nitrogen-rich salts show higher thermal stabilities, especially the guanidinium salt (198 °C).[108] Although the neutral compound is less thermally stable than **3**, its nitramine is seemingly better suited for the

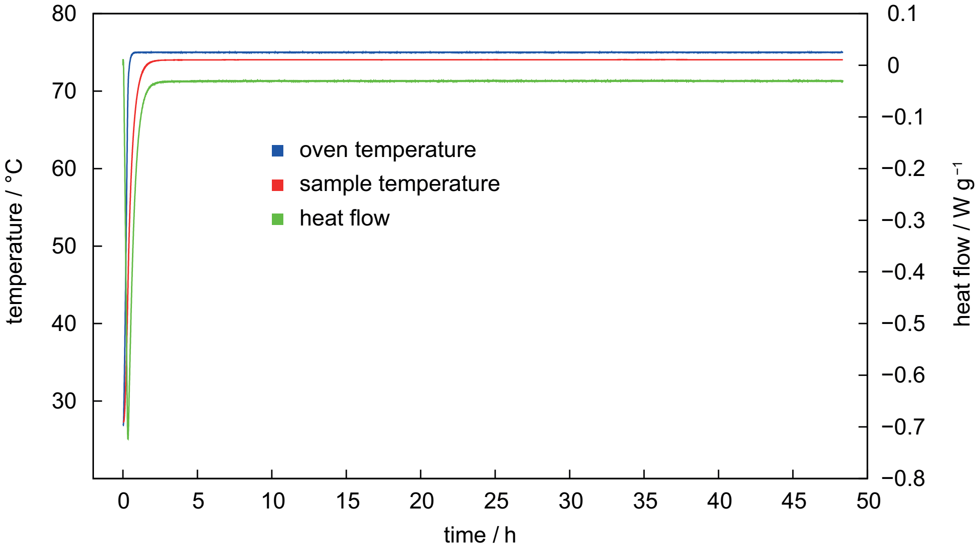


Figure 2.10: Isoperibolic long term measurement (48 hours) of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**).

raised electron density and compensation of its own lower stability when compared to the nitro group of **3**, regarding this special case with an azide as the second functional group.

2.2.5 Sensitivities

For initial safety testing the impact and friction sensitivities as well as the electrostatic sensitivities were determined and assigned according to the UN recommendations on the transport of dangerous goods. The parent compound **3** is less sensitive to impact (5 J) than expected due to the fact that it is an azole based compound incorporating an azide besides a nitro group, although it still has to be qualified as sensitive. The friction sensitivity is clearly higher (42 N) and **3** should therefore only be handled with care. Methylation yielding **4** drastically lowers the sensitivities ($>$ 40 J, 288 N). While the monohydrated sodium salt (**5**) is "only" sensitive (3 J, 144 N), the other metal salts are very sensitive primary explosives, both concerning their nature and their sensitivities. All show impact sensitivities of $<$ 1 J and could already be detonated by a hit with a small hammer. The friction sensitivities are similarly high with $<$ 5 N, except for the monohydrate **9** (7 N). While the ammonium (**10**) and aminoguanidinium (**12**) salts are also rather sensitive to impact with 3 and 7 J, respectively, the guanidinium salt **11** is almost insensitive (30 J). Compound **10** displays the highest friction sensitivity of the three nitrogen-rich salts (144 N), with **11** and **12** being comparably rather less sensitive (288 and 240 N, respectively). The commonly used secondary explosive RDX is also classified as sensitive to both impact and friction (7.4 J, 120 N). Concerning the sensitivity to electrostatic discharge, compound **3** shows the highest among the neutral and nitrogen-rich compounds (50 mJ). The others range between 200

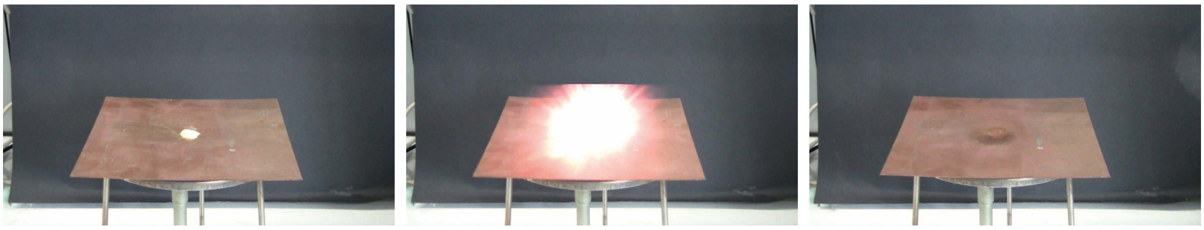


Figure 2.11: Hot-plate test of potassium 5-azido-3-nitro-1,2,4-triazolate (**6**, 200 mg) on a copper plate, heated with a Bunsen burner. A deep dent is visible in the former place of the substance.

(**4**) and 500 mJ (**10** and **11**), including the sodium salt **5**. These findings are in agreement to those observed for RDX (200 mJ). The metal salts **6**, **7** and **8** are far more sensitive, being between 3 (**8**) and 15 mJ (**6**) and therefore in the range of primary explosives like lead azide (5 mJ). Furthermore, compounds **6**, **7**, **8** and **9** were the only ones to always detonate (impact, friction and electrostatic discharge), while the other compounds merely only vanished without sound.

2.2.6 Energetic Properties

The metal salts containing the cations sodium (**5**), potassium (**6**), cesium (**7**), silver (**8**) and lead (**9**) were the main focus of this study and therefore tested for their capability of being primary explosives. Compounds **8** and **9** have only comparative character, due to the already mentioned toxicity and sensitivity reasons. A small amount (approx. 5 mg) of **5**–**9** was heated on a spatula by a lighter, without direct flame contact. Except for the hydrated **5** all compounds detonated upon reaching their corresponding ignition temperatures. Compound **6** was further tested with the hot-plate test, in which 200 mg were placed on a 2 mm thick copper plate and heated with a Bunsen burner from below (again without direct flame contact). Upon reaching its ignition temperature the compound detonated violently, leaving no solid residues (see figure 2.11). Next, a small sample (again approx. 5 mg) of **6**–**8** was fixed to a surface with a bit of transparent tape and poked with a preheated needle. Unfortunately, in this case the compounds showed no sing of a DDT and were merely only deflagrating, although very fast. Nevertheless, the potassium salt **6** was tested for its capability to initiate the commonly used secondary explosive RDX. Thus, about 400 mg of RDX were loaded in a copper tube (6.50 mm × 57.70 mm), layered with a varying amount of **6** (10, 25, 50, 75, or 100 mg) and slightly pressed. For the ignition a commercial type A electrical igniter was used on top.[109] Figure 2.12 shows the copper tube before and after the experiment with 10 mg of **6** as the primary explosive. Full initiation of RDX without the primary explosive, using only the igniter, is not possible. The results reveal **6** and the similarly performing cesium salt **7** as interesting materials for further testing.

Table 2.3: Energetic properties of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**), its methylated derivative **4** and salts **5**–**12**.

Compound	IS / J	FS / N	ESD / mJ	T_d / °C	DDT	fast heating
3	5	42	50	149	—	—
4	40	288	200	137	—	—
5	3	144	300	148	no	—
6	1	5	15	152	yes	deflagration
7	1	5	7	185	yes	deflagration
8	1	5	3	149	yes	deflagration
9	1	8	—	130	yes	deflagration
10	3	144	500	139	—	—
11	30	288	500	160	—	—
12	7	240	400	138	—	—

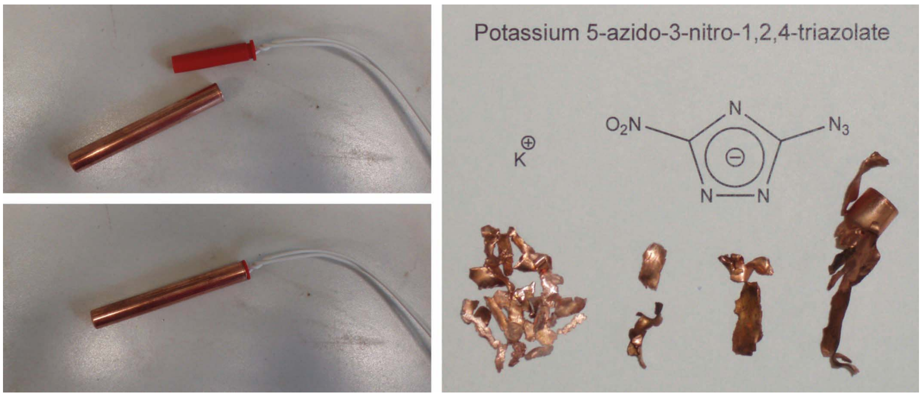


Figure 2.12: Copper tube initiation test of potassium 5-azido-3-nitro-1,2,4-triazolate (**6**) (400 mg RDX, 10 mg **6**). Left: test setup; right: collected fragments after detonation.

An application of the anion in nitrogen-rich ionic secondary explosives is unlikely due to low densities (**11**: 1.50 $\mathrm{g\,cm^{-3}}$), which should be at least 1.78 $\mathrm{g\,cm^{-3}}$ to be able to compete with RDX, and especially due to the low thermal stabilities of the presented salts **10**–**12**. Higher energetic cations like hydroxylammonium or triaminoguanidinium always exhibit lower stabilities than ammonium (**10**) or aminoguanidinium (**12**), and would thus be far below the general requirement of 180 °C.

2.2.7 Toxicity Assessment

To assess the toxicity of **3** and its anion to aquatic life, diluted aqueous solutions of the compounds were subjected to the luminescent marine bacterium *Aliivibrio fischeri*, a representative species for other aquatic life, using the Microtox® method with the commercially available bioassay system Lange LUMIStox.[110–112] Being the most important toxicological parameter, the EC_{50} value of the sample was determined. EC_{50} is the effective concentration of the examined compound at which the bioluminescence of the strain *Aliivibrio fischeri* is decreased by 50 % after a defined period of exposure when compared to the original bioluminescence of the sample before being treated with the differently diluted solutions of the test compound. For RDX a value of $322\,\mu g\,mL^{-1}$ is observed after an incubation time of 15 minutes and $266\,\mu g\,mL^{-1}$ after 30 minutes.[110] While **3** displays EC_{50} values of $421\,\mu g\,mL^{-1}$ (15 minutes) and $362\,\mu g\,mL^{-1}$ (30 minutes), compound **6** was determined with $2283\,\mu g\,mL^{-1}$ (15 minutes) and $1065\,\mu g\,mL^{-1}$ (30 minutes), making both compounds slightly less toxic than RDX to *Aliivibrio fischeri*. The values are comparable to 1,4-dimethyl-5-aminotetrazolium azide ($512\,\mu g\,mL^{-1}$ for 15 minutes and $435\,\mu g\,mL^{-1}$ for 30 minutes) or guanidinium 5-nitrotetrazolate ($1383\,\mu g\,mL^{-1}$ for 15 minutes and $784\,\mu g\,mL^{-1}$ for 30 minutes) and much less toxic than bis(1*H*-tetrazol-5-yl)amine ($14\,\mu g\,mL^{-1}$ for 15 minutes and $15\,\mu g\,mL^{-1}$ for 30 minutes).[110]

2.3 Conclusions

The goal of the present study has been the preparation and comprehensive characterization of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) and selected metal and nitrogen-rich salts with sodium (**5**), potassium (**6**), cesium (**7**), silver (**8**), lead (**9**), ammonium (**10**), guanidinium (**11**) and aminoguanidinium (**12**). Utilization of single crystal X-ray diffraction revealed the structure of several of the investigated compounds (**3**, **4**, **6**, **9**). The thermal stabilities of the compounds are unfortunately rather low between 130 (**9**) and 185 °C (**7**). The toxicity of **3** and **6** was assessed with the Microtox® method, revealing both as less toxic to *Aliivibrio fischeri* than RDX. The salts with potassium (**3**) and cesium (**7**) were identified as interesting new primary explosives. Both are able to undergo a DDT upon heating on a spatula. The initiation capability of **6** was thus tested with RDX, with even as few as 10 mg of substance being able to initiate the secondary explosive.

2.4 Experimental Part

Ammonium 3,5-dinitro-1,2,4-triazolate (1)

A dropping funnel without pressure-equalizer was charged with 3,5-diamino-1*H*-1,2,4-triazole (10.0 g, 100 mmol) in sulfuric acid (0.75 M, 310 mL), which was slowly added drop wise to an ice cooled and vigorously stirred solution of sodium nitrite (69.0 g, 1.00 mol) in water (300 mL) in a 2 L three necked round flask. After the addition, which should take about two hours, the resulting orange suspension was heated to 70 °C until a clear orange to red solution was formed. It was then cooled again with an ice bath and sulfuric acid (30 %, 150 mL) was added, followed by the addition of urea (3 g) in small portions. After stirring overnight at room temperature the mixture was extracted with ethyl acetate (6 × 200 mL). The combined organic phases were dried over magnesium sulfate and concentrated under reduced pressure to a viscous yellow oil. It was dissolved in water (10 mL), basified with aqueous ammonia solution (12.5 %, 22 mL), layered with diethyl ether and stored overnight at 4 °C. The resulting precipitate was filtered off and washed with a small amount of water and ethanol to yield yellow to orange crystals (17.1 g, 88.1 mmol, 88 %). ^{1}H NMR (DMSO-d_6): δ = 7.09 (br, NH_4^+). ^{13}C NMR (DMSO-d_6): δ = 162.9. ^{14}N NMR (DMSO-d_6): δ = −16 (NO_2), −354 (NH_4^+). IR (ATR): $\tilde{\nu}$ = 3588 (m), 3291 (m), 3170 (m), 3044 (m), 2854 (m), 2465 (w), 2363 (w), 1636 (w), 1536 (s), 1496 (s), 1449 (vs), 1389 (vs), 1352 (vs), 1300 (vs), 1110 (m), 1049 (m), 844 (vs), 832 (s), 768 (w), 684 (m), 645 (s) cm^{-1}. EA ($C_2H_4N_6O \cdot H_2O$): calculated C 12.38, H 3.12, N 43.30 %; found C 11.78, H 3.27, N 39.51 %.

5-Amino-3-nitro-1*H*-1,2,4-triazole (2)

A mixture of **1** (19.4 g, 100 mmol) and hydrazine monohydrate (26 mL, 0.54 mol) was stirred for three hours at 80 °C. The cooled down orange solution was mixed with water (37 mL) and acidified with hydrochloric acid (37 %, 37 mL). After stirring the yellow solution overnight at room temperature the resulting precipitate was filtered off and washed with a very small amount of water, then dried overnight at 70 °C to yield a yellow powder (9.26 g, 71.7 mmol, 72 %). ^{1}H NMR (DMSO-d_6): δ = 13.14 (s, 1H, NH), 6.80 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ = 160.9 (C1), 157.4 (C2). ^{14}N NMR (DMSO-d_6): δ = −18 (NO_2). IR (ATR): $\tilde{\nu}$ = 3434 (m), 3323 (m), 3164 (m), 3005 (m), 1629 (vs), 1572 (m), 1507 (vs), 1383 (s), 1300 (vs), 1143 (m), 1078 (m), 1036 (m), 1013 (s), 957 (w), 838 (s), 801 (w), 756 (m), 721 (m) cm^{-1}. EA ($C_2H_3N_5O_2$): calculated C 18.61, H 2.34, N 54.26 %; found C 18.85, H 2.28, N 54.21 %.

5-Azido-3-nitro-1*H*-1,2,4-triazole (3)

Sodium nitrite (379 mg, 5.50 mmol) was added to a stirred suspension of **2** (645 mg, 5.00 mmol) in sulfuric acid (25 %, 30 mL) at 0 to 5 °C in small portions and the resulting yellow solution was stirred for one hour at room temperature. After the addition of a small amount of urea, sodium azide (390 mg, 6.00 mmol) was added in small portions, followed by stirring for further 30 minutes. The reaction mixture was extracted with ethyl acetate (3 × 20 mL), the combined organic phases were dried over magnesium sulfate and evaporated to dryness under reduced pressure. The residue was stirred in *n*-pentane overnight, filtered and washed with *n*-pentane to yield a colorless powder (685 mg, 4.42 mmol, 88 %). ^{1}H NMR (CD_3CN): δ = 10.74 (br). ^{1}H NMR (DMSO-d_6): δ = 9.73 (br). ^{13}C NMR (DMSO-d_6): δ = 160.3 (C1), 151.8 (C2). ^{14}N NMR (DMSO-d_6): δ = −22 (N4), −141 (N6). ^{15}N NMR

(DMSO-d_6): $\delta = -20.9$ (N4), -91.6 (N2), -137.0 (N7), -139.9 (N6), -154.0 (N3), -172.7 (N1), -285.9 (N5). IR (ATR): $\tilde{\nu} = 3198$ (m), 2367 (w), 2219 (w), 2148 (s), 1670 (w), 1630 (w), 1569 (m), 1525 (vs), 1489 (vs), 1443 (s), 1417 (s), 1378 (s), 1294 (s), 1187 (vs), 1165 (s), 1053 (m), 1035 (s), 1010 (m), 843 (vs), 787 (vs), 766 (s), 706 (vs) $\mathrm{cm^{-1}}$. Raman (300 mW): $\tilde{\nu} = 2159$ (9), 1543 (16), 1492 (100), 1422 (17), 1384 (25), 1369 (9), 1320 (6), 1299 (10), 1169 (17), 1037 (14), 1012 (5) $\mathrm{cm^{-1}}$. MS (DEI+): $m/z = 155.1$ ($[\mathrm{M}]^+$). EA ($C_2HN_7O_2$): calculated C 15.49, H 0.65, N 63.23 %; found C 15.37, H 0.90, N 59.98 %. DSC ($5\,\mathrm{°C\,min^{-1}}$): $T_\mathrm{m} = 110\,°\mathrm{C}$, $T_\mathrm{d} = 149\,°\mathrm{C}$. Sensitivities (grain size $< 100\,\mu\mathrm{m}$): IS 5 J, FS 42 N, ESD 50 mJ.

5-Azido-1-methyl-3-nitro-1,2,4-triazole (4)

Dimethyl sulfate (1.26 g, 10.0 mmol) was added drop wise to **3** (1.55 g, 10.0 mmol) and sodium hydroxide (800 mg, 20.0 mmol) in water (10 mL). The reaction mixture was then stirred overnight at 105 °C. The precipitate obtained after cooling to room temperature was filtered off and washed with a small amount of water to yield fine colorless needles suitable for X-ray diffraction (270 mg, 1.60 mmol, 16 %). ^{1}H NMR (DMSO-d_6): $\delta = 3.74$ (s, CH_3). ^{13}C NMR (DMSO-d_6): $\delta = 158.7$ (C1), 150.3 (C2), 35.4 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -23$ (N4), -142 (N6). ^{15}N NMR (DMSO-d_6): $\delta = -22.6$ (N4), -83.3 (q, $^3J_\mathrm{NH} = 2.03\,\mathrm{Hz}$, N2), -137.9 (N7), -141.6 (N6), -153.9 (N3), -184.6 (q, $^2J_\mathrm{NH} = 2.11\,\mathrm{Hz}$, N1), -288.7 (N5). IR (ATR): $\tilde{\nu} = 2394$ (w), 2294 (w), 2166 (s), 1551 (s), 1502 (vs), 1449 (s), 1398 (s), 1311 (vs), 1266 (s), 1252 (vs), 1044 (m), 1020 (m), 875 (s), 811 (s), 708 (s), 683 (s), 642 (m) $\mathrm{cm^{-1}}$. Raman (300 mW): $\tilde{\nu} = 2960$ (28), 2160 (11), 1551 (12), 1535 (52), 1499 (54), 1453 (39), 1398 (100), 1303 (32), 1271 (13), 1253 (28), 1046 (24), 1023 (12), 769 (6), 683 (13) $\mathrm{cm^{-1}}$. MS (DEI+): $m/z = 169.0$ ($[\mathrm{M}]^+$). EA ($C_3H_3N_7O_2$): calculated C 21.31, H 1.79, N 57.98 %; found C 21.58, H 1.80, N 56.59 %. DSC ($5\,\mathrm{°C\,min^{-1}}$): $T_\mathrm{m} = 115\,°\mathrm{C}$, $T_\mathrm{d} = 137\,°\mathrm{C}$. Sensitivities (grain size 100 to 500 µm): IS > 40 J, FS 288 N, ESD 200 mJ.

Sodium 5-azido-3-nitro-1,2,4-triazolate monohydrate (5)

Sodium carbonate (265 mg, 2.50 mmol) and **3** (853 mg, 5.50 mmol) were refluxed in ethanol (60 mL) until a clear yellow solution was obtained. The solvent was evaporated under reduced pressure and the residue was stirred in diethyl ether to remove excess **3**, filtered off and washed with diethyl ether to yield a yellow powder (885 mg, 4.45 mmol, 91 %). ^{1}H NMR (DMSO-d_6): $\delta = 3.46$ (H_2O). ^{13}C NMR (DMSO-d_6): $\delta = 163.8$ (C1), 155.9 (C2). ^{14}N NMR (DMSO-d_6): $\delta = -14$ (N4), -133 (N6). IR (ATR): $\tilde{\nu} = 3497$ (w), 3299 (w), 2423 (w), 2270 (w), 2150 (s), 1680 (w), 1545 (s), 1496 (m), 1451 (vs), 1395 (s), 1340 (vs), 1295 (s), 1217 (s), 1096 (s), 1055 (w), 1026 (w), 850 (s), 804 (m), 729 (m), 656 (s) $\mathrm{cm^{-1}}$. Raman (300 mW): $\tilde{\nu} = 2158$ (15), 1539 (11), 1459 (45), 1395 (94), 1339 (100), 1297 (10), 1220 (7), 1099 (97), 1028 (13) cm^{-1}. MS (FAB+): m/z = 23.0 ([Na]$^+$). MS (FAB−): m/z = 154.0 ([$C_2N_7O_2$]$^-$). EA ($C_2N_7NaO \cdot H_2O$): calculated C 12.31, H 1.03, N 50.26 %; found C 12.82, H 0.96, N 49.96 %. DSC (5 °C min^{-1}): T_{dh} = 87 °C, T_d = 148 °C. Sensitivities (grain size < 100 µm): IS 3 J, FS 144 N, ESD 300 mJ.

Potassium 5-azido-3-nitro-1,2,4-triazolate (6)

Potassium carbonate (138 mg, 1.00 mmol) and **3** (341 mg, 2.20 mmol) were refluxed in ethanol (24 mL) until a clear yellow solution was obtained. The solvent was evaporated under reduced pressure and the residue was stirred in diethyl ether, filtered off and washed with diethyl ether to yield a yellow powder (315 mg, 1.63 mmol, 82 %). ^{13}C NMR (DMSO-d_6): δ = 163.9 (C1), 156.2 (C2). ^{14}N NMR (DMSO-d_6): δ = −12 (N4), −134 (N6). ^{15}N NMR (DMSO-d_6): δ = −12.4 (N4), −48.5 (N2), −67.2 (N1), −130.4 (N6), −140.4 (N7), −152.8 (N3), −288.5 (N5). IR (ATR): $\tilde{\nu}$ = 2444 (w), 2243 (w), 2142 (s), 1531 (s), 1478 (m), 1441 (vs), 1386 (s), 1324 (vs), 1286 (m), 1226 (m), 1084 (s), 1054 (w), 1018 (w), 843 (m), 796 (w), 731 (m), 656 (m) cm^{-1}. Raman (300 mW): $\tilde{\nu}$ = 2153 (4), 1457 (11), 1445 (28), 1387 (44), 1323 (72), 1083 (100), 1019 (5) cm^{-1}. MS (FAB+): m/z = 38.9 ([K]$^+$). MS (FAB−): m/z = 154.0 ([$C_2N_7O_2$]$^-$). EA ($C_2KN_7O_2$): calculated C 12.44, N 50.76 %; found C 13.28, N 50.00 %. DSC (5 °C min^{-1}): T_d = 152 °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 15 mJ.

Cesium 5-azido-3-nitro-1,2,4-triazolate (7)

Cesium carbonate (326 mg, 1.00 mmol) and **3** (341 mg, 2.20 mmol) were refluxed in ethanol (24 mL) and a few drops of water until a clear yellow solution was obtained. A very small amount of water and little more ethanol were added to the residue after removal of the solvent under reduced pressure. The solid was filtered off and washed with diethyl ether to yield a yellow powder (504 mg, 1.76 mmol, 88 %). ^{13}C NMR (DMSO-d_6): δ = 163.7 (C1), 155.7 (C2). ^{14}N NMR (DMSO-d_6): δ = −15 (N4), −134 (N6). IR (ATR): $\tilde{\nu}$ = 2446 (w), 2363 (w), 2339 (w), 2264 (w), 2216 (w), 2150 (m), 2130 (m), 1512 (s), 1474 (vs), 1436 (vs), 1387 (s), 1330 (s), 1292 (m), 1226 (m), 1080 (s), 1036 (w), 844 (m), 782 (w), 727 (m), 660 (w) cm^{-1}. Raman (300 mW): $\tilde{\nu}$ = 1435 (21), 1384 (41), 1330 (77), 1076 (100), 1014 (6) cm^{-1}. MS (FAB+): m/z = 133.0 ([Cs]$^+$). MS (FAB−): m/z = 154.0 ([$C_2N_7O_2$]$^-$). EA ($C_2CsN_7O_2$): calculated C 8.37, N 34.17 %; found C 8.66, N 33.73 %. DSC (5 °C min^{-1}): T_d = 185 °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 7 mJ.

Silver 5-azido-3-nitro-1,2,4-triazolate (8)

Silver nitrate (170 mg, 1.00 mmol) in water (20 mL) was added drop wise to **3** (155 mg, 1.00 mmol) in water (40 mL) and the resulting suspension was stirred in the dark for 30 minutes. The precipitate was filtered off and washed with water and ethanol to yield a pale yellow powder (174 mg, 664 µmol, 66 %). IR (ATR): $\tilde{\nu}$ = 2429 (w), 2141 (s), 1553 (m), 1493 (s), 1467 (vs), 1403 (m), 1347 (m), 1307 (s), 1220 (s), 1116 (m), 1104 (m), 846 (m), 798 (m), 718 (w) cm^{-1}. Raman (300 mW): $\tilde{\nu}$ = 2141 (7), 1541 (6), 1492 (4), 1460 (57), 1407 (30), 1347 (100), 1310 (5), 1118 (15), 1105 (28), 1046 (7) cm^{-1}. MS (DEI+): m/z = 106.9 ($[Ag]^+$). EA ($C_2AgN_7O_2$): calculated C 9.17, N 37.43 %; found C 9.62, N 36.73 %. DSC (5 °C min^{-1}): $T_d = 149\,°C$. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 3 mJ.

Lead bis(5-azido-3-nitro-1,2,4-triazolate) monohydrate (9)

Lead nitrate (365 mg, 1.10 mmol) in water (20 mL) was added drop wise to **3** (310 mg, 2.00 mmol) in hot water (40 mL) and sodium hydroxide solution (2 M, 1.0 mL, 2.0 mmol). Yellow single crystals precipitated after several weeks. The yield was not determined. IR (ATR): $\tilde{\nu}$ = 3297 (w), 2154 (s), 1530 (m), 1450 (vs), 1386 (s), 1328 (s), 1294 (s), 1223 (m), 1212 (m), 1100 (s), 1064 (m), 1019 (m), 844 (m), 805 (m), 720 (m) cm^{-1}. EA ($C_4N_{14}PbO_4 \cdot H_2O$): calculated C 9.01, H 0.38, N 36.77 %; found C 9.25, H 0.43, N 35.66 %. DSC (5 °C min^{-1}): $T_d = 130\,°C$. Sensitivities (grain size < 100 µm): IS < 1 J, FS 8 N.

Ammonium 5-azido-3-nitro-1,2,4-triazolate (10)

Aqueous ammonia solution (2 M, 3.0 mL, 6.0 mmol) and **3** (853 mg, 5.50 mmol) were stirred in ethanol (40 mL) for 30 minutes. The solvent was evaporated under reduced pressure and the residue was stirred in diethyl ether, filtered off and washed with diethyl ether to yield a yellow powder (695 mg, 4.04 mmol, 74 %). ^1H NMR (DMSO-d_6): δ = 7.19 (NH_4^+). ^{13}C NMR (DMSO-d_6): δ = 163.6 (C1), 155.9 (C2). ^{14}N NMR (DMSO-d_6): δ = −15 (N4), −133 (N6), −354 (NH_4^+). IR (ATR): $\tilde{\nu}$ = 3333 (w), 3135 (w), 2948 (w), 2757 (w), 2465 (w), 2135 (s), 1685 (w), 1533 (w), 1486 (m), 1445 (vs), 1423 (vs), 1393 (vs), 1341 (vs), 1297 (s), 1235 (s), 1090 (vs), 1065 (w), 1052 (w), 1029 (w), 842 (s), 801 (m), 726 (m), 655 (s) cm^{-1}. Raman (300 mW): $\tilde{\nu}$ = 2139 (4), 1454 (28), 1395 (38), 1335 (72), 1090 (100), 1031 (7) cm^{-1}. MS (FAB+): m/z = 18.1 ($[NH_4]^+$). MS (FAB−): m/z = 154.0 ($[C_2N_7O_2]^-$). EA ($C_2H_4N_8O_2$): calculated C 13.96, H 2.34, N 64.11 %; found C 14.38, H 2.30, N 64.61 %. DSC (5 °C min^{-1}): $T_m = 139\,°C$ (equals T_d). Sensitivities (grain size < 100 µm): IS 3 J, FS 144 N, ESD 500 mJ.

Guanidinium 5-azido-3-nitro-1,2,4-triazolate (11)

Guanidinium carbonate (815 mg, 2.50 mmol) and **3** (853 mg, 5.50 mmol) were refluxed in ethanol (60 mL) and a few drops of water until a clear yellow solution was obtained. The solvent was evaporated under reduced pressure and the residue was stirred in diethyl ether, filtered off and washed with diethyl ether to yield a yellow powder (1.03 g, 4.81 mmol, 96 %). ^{1}H NMR (DMSO-d_6): $\delta = 6.92$ (NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 163.7$ (C1), 157.9 (G^+), 155.7 (C2). ^{14}N NMR (DMSO-d_6): $\delta = -15$ (N4), -133 (N6). IR (ATR): $\tilde{\nu} = 3476$ (m), 3348 (w), 3079 (m), 2440 (w), 2254 (w), 2143 (vs), 1688 (m), 1654 (s), 1574 (w), 1518 (m), 1477 (vs), 1445 (vs), 1396 (s), 1335 (vs), 1300 (m), 1227 (m), 1143 (w), 1087 (vs), 1045 (w), 1027 (w), 1007 (w), 841 (s), 786 (w), 719 (w), 655 (w), 624 (w) cm^{-1}. Raman (300 mW): $\tilde{\nu} = 2154$ (2), 1520 (6), 1483 (5), 1451 (29), 1397 (40), 1337 (78), 1088 (100), 1030 (5), 1009 (11), 843 (13) cm^{-1}. MS (FAB+): $m/z = 60.0$ ($[CH_6N_3]^+$). MS (FAB−): $m/z = 154.0$ ($[C_2N_7O_2]^-$). EA ($C_3H_6N_{10}O_2$): calculated C 16.83, H 2.82, N 65.41 %; found C 17.18, H 2.73, N 64.77 %. DSC (5 °C min^{-1}): $T_d = 160$ °C. Sensitivities (grain size < 100 µm): IS 30 J, FS 288 N, ESD 500 mJ.

Aminoguanidinium 5-azido-3-nitro-1,2,4-triazolate (12)

Aminoguanidinium hydrogen carbonate (681 mg, 5.00 mmol) and **3** (853 mg, 5.50 mmol) were refluxed in ethanol (60 mL) until a clear yellow solution was obtained. After filtration the solvent was evaporated under reduced pressure and the residue was stirred in diethyl ether, filtered off and washed with diethyl ether to yield a pale yellow powder (1.06 g, 4.62 mmol, 92 %). ^{1}H NMR (DMSO-d_6): $\delta = 8.58$ (s, 1H, NH), 7.27 (s, 2H, C−NH_2), 6.77 (s, 2H, C−NH_2), 4.69 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 163.7$ (C1), 158.8 (AG^+), 155.8 (C2). ^{14}N NMR (DMSO-d_6): $\delta = -15$ (N4), -133 (N6). IR (ATR): $\tilde{\nu} = 3435$ (w), 3326 (w), 3138 (w), 2425 (w), 2128 (s), 1669 (s), 1526 (m), 1479 (s), 1442 (vs), 1397 (m), 1334 (s), 1300 (s), 1222 (m), 1084 (s), 1043 (w), 990 (w), 953 (w), 920 (m), 839 (s), 782 (w), 728 (w), 656 (m), 621 (w) cm^{-1}. Raman (300 mW): $\tilde{\nu} = 2143$ (4), 1464 (26), 1443 (8), 1397 (42), 1337 (91), 1089 (100), 1024 (8), 842 (5) cm^{-1}. MS (FAB+): $m/z = 75.0$ ($[CH_7N_4]^+$). MS (FAB−): $m/z = 154.0$ ($[C_2N_7O_2]^-$). EA ($C_3H_7N_{11}O_2$): calculated C 15.72, H 3.08, N 67.23 %; found C 16.19, H 2.92, N 66.75 %. DSC (5 °C min^{-1}): $T_m = 138$ °C (equals T_d). Sensitivities (grain size < 100 µm): IS 7 J, FS 240 N, ESD 400 mJ.

5-Azido-1*H*-1,2,4-triazole-3-carbonitrile

D. Izsák, T. M. Klapötke, S. Reuter, T. Rösener
Z. Anorg. Allg. Chem. **2013**, *639*, 899–905.

3.1 Introduction

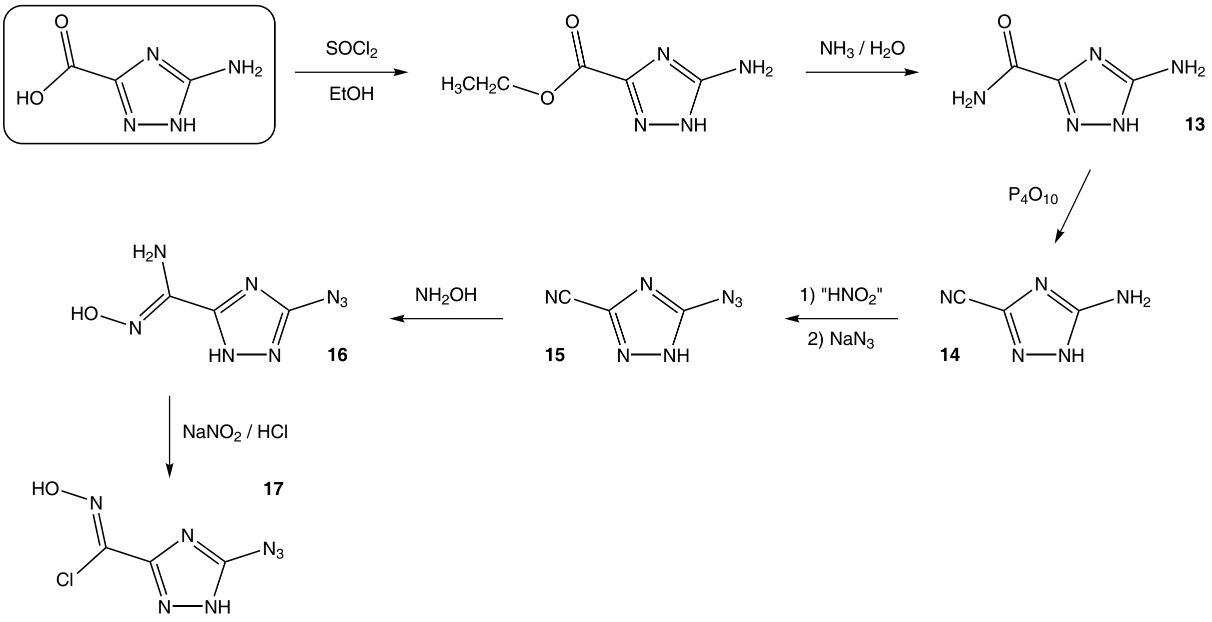
A recently investigated possibility to increase the enthalpy of formation of nitrogen-rich azoles are the cyano and the carboxamidoxime groups.[113,114] As mentioned in the introduction, the enthalpy of formation is one of the most important parameters for both primary and secondary explosives. Additionally, the cyano group also features both a negative inductive and mesomeric effect similar to the nitro group, albeit not as strong. As demonstrated with 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) in chapter 2 the nitro group seems to be better suited to stabilize the anion in salts in comparison to 3-azido-1*H*-1,2,4-triazole (**50**) and 3,5-diazido-1*H*-1,2,4-triazole,[56] with several of its salts having a higher thermal stability than the neutral compound **3** itself. Furthermore nitriles can be employed as precursor molecules for tetrazoles,[115] making 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) a viable compound for further research.

Thus, the goal of the present study has been the combination of the azido group with a nitrile, and the nitrile based carboxamidoxime, on a 1,2,4-triazole backbone and the investigation of the applicability of the resulting **15** and its derivative 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**) as primary explosives.

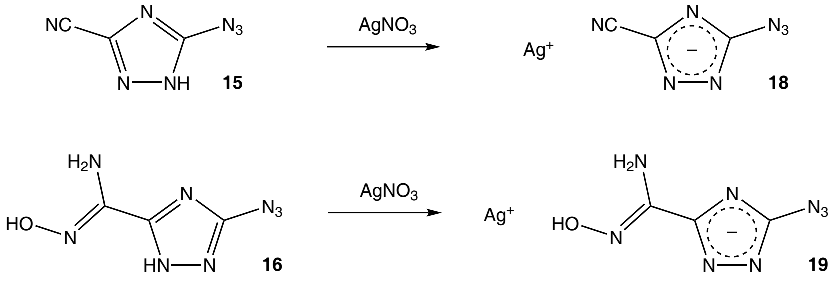
3.2 Results and Discussion

3.2.1 Syntheses

The starting material 3-amino-1*H*-1,2,4-triazole-5-carboxamide (**13**) was synthesized by the reaction of thionyl chloride with 3-amino-1*H*-1,2,4-triazole-5-carboxylic acid in ethanol and the subsequent ammonolysis of the thus formed ester in 25 % ammonia solution. Although **13** can be dehydrated by various dehydration agents (thionyl chloride, phosphoryl chloride) in dry pyridine to yield 5-amino-1*H*-1,2,4-triazole-3-carbonitrile (**14**), the best route is by using phosphorous pentoxide in dry acetonitrile at room temperature. 5-Azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) was then prepared by diazotation of **14** with sodium nitrite in 20 % sulfuric acid and subsequent reaction with sodium azide. 5-Azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**) was prepared similarly to literature methods by the reaction



Scheme 3.1: Synthetic pathway for 5-azido-1H-1,2,4-triazole-3-carbonitrile (**15**), 3-azido-1H-1,2,4-triazole-5-carboxamidoxime (**16**) and 5-azido-1H-1,2,4-triazole-3-carbohydroximoyl chloride (**17**) from commercially available 3-amino-1H-1,2,4-triazole-5-carboxylic acid.



Scheme 3.2: Synthesis of the silver salts **18** and **19** of 5-azido-1H-1,2,4-triazole-3-carbonitrile (**15**) and 3-azido-1H-1,2,4-triazole-5-carboxamidoxime (**16**), respectively.

of **15** with hydroxylamine in refluxing water, subsequent cooling to room temperature, acidification with hydrochloric acid and diazotation with excess sodium nitrite.[116,117] 3-Azido-1H-1,2,4-triazole-5-carboxamidoxime (**16**) is the intermediate of this reaction and can be isolated when ethanol or isopropanol is used instead of water, but the yields were lower and it was hard to purify due to its good solubility.

The silver salts of **15** and **16** (**18** and **19**, respectively) were prepared by the reaction of the neutral compound with silver nitrate in water.

3.2.2 Crystal Structure Analysis

The structure (bond lengths and angles) of the 1,2,4-triazole backbone of all three compounds **15**, **16** and **17** and their azide moieties are in accordance with similar structures reported

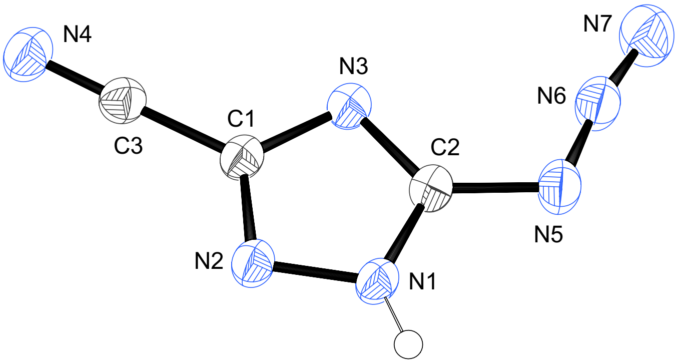


Figure 3.1: Molecular structure of 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**). Thermal ellipsoids at 50 % probability.

in the literature,[102,107,108] and so are the remaining bonds.[118]

5-Azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) crystallized in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. It is notable that the anion of **15** is a new binary C-N compound. While the triazole ring itself is planar the azide is slightly twisted out of the plane by 9.4(2)°. The molecular structure is shown in figure 3.1. The bonds of the nitrile (C1–C3: 1.441(2) Å; N4–C3: 1.144(2) Å) are both slightly longer than those reported for 2*H*-tetrazole-5-carbonitrile (C1–C2: 1.438(4) Å; N5–C2: 1.138(4) Å) recently.[113] The molecules are forming dimers, which further form infinite chains, linked by two bifurcated hydrogen bonds (figure 3.2, table 3.1). Interestingly the chains are not forming a simple two dimensional layer structure, like the also planar 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) does, but rather a complex three dimensional one with two types of layers. Both layers are similar, but with different orientations. The distance between the layers is approximately 3.29 Å in both types. The chains of the second layer type are intertwined between two parallel chains of the first layer. The main characteristical connection between the two types is a quite directed $N_\gamma \cdots N_\beta$ interaction between two azides ($N7\cdots N6^{vi}$: 3.089(2) Å; $N6–N7\cdots N6^{vi}$: 131.2(1)°) below the sum of the van der Waals radii ($\sum r_\mathrm{w}(\mathrm{N,N}) = 3.10$ Å).[104] This type of contact is quite common in literature known compounds but almost never mentioned. Examples include hydrazoic acid itself,[119] the very sensitive diazido glyoxime,[120] various organic azides,[121,122] binary azides of arsenic and tellurium,[123,124] binary azides of group 5 transition metals,[125] or a similar azido-1,2,4-triazole like 5-amino-3-azido-1*H*-1,2,4-triazole.[126] The structure features a second short contact ($N7\cdots C2^{v}$: 3.078(2) Å) below the sum of the van der Waals radii ($\sum r_\mathrm{w}(\mathrm{C,N}) = 3.25$ Å),[104] again involving the azide gamma nitrogen atom. Both contacts are illustrated in figure 3.3. The contacts are probably only of an electrostatic nature due to their length being only slightly under the sum of the van der Waals radii. For example according to valence bond structural discussions for 5-azido-1*H*-tetrazole those individual Lewis type structures are of higher importance in

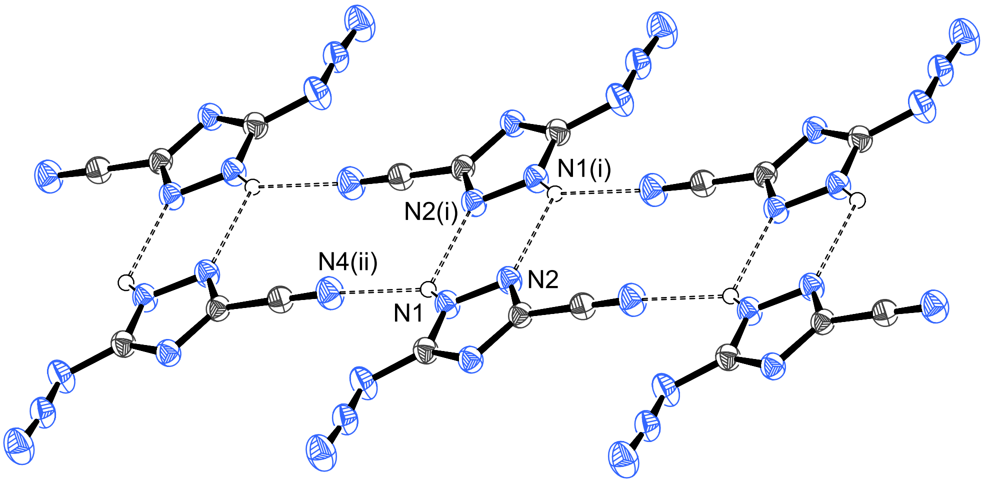


Figure 3.2: Hydrogen bonds of 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**), forming chains of dimers. Thermal ellipsoids at 50 % probability.

Table 3.1: Hydrogen bonds present in 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**).

D–H···A	*d*(D–H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠(D–H···A) / °
N1–H71···O1^{i}	0.84(2)	2.43(2)	2.993(2)	126(1)
N1–H71···N4^{ii}	0.84(2)	2.29(2)	3.011(2)	144(1)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x+1, y-1, z$.

which the beta nitrogen atom bears a positive formal charge, while the alpha or gamma atoms bear a negative one.[127] For a possible explanation of these electrostatic interactions in the solid state the Mulliken and NBO charges were calculated on an optimized gas phase structure (B3LYP/cc-pVTZ), illustrated in figure 3.4. Considering the Mulliken charges, C2 and especially N6 are strongly positive, while N5 is strongly negative and N7 only slightly negative. The more reasonable NBO charges follow a similar trend but here N7 bears a slightly positive charge. The true charge distribution is probably somewhere in between because those of the calculation are for isolated molecules in the gas phase which are uninfluenced by packing effects occurring in the solid state.

3-Azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**) crystallized in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular structure is shown in figure 3.5. Interestingly the azide is rotated by 180° (and this time in plane with the ring) and the proton is shifted to the former N2 position, when compared most of the structures in this work and the literature,[106] similar to 3-azido-1*H*-1,2,4-triazole.[128] The bonding situation of the carboxamidoxime (C2–C3: 1.468(3) Å; N7–C3: 1.284(3) Å; N8–C3: 1.344(2) Å; O1–N7: 1.424(2) Å) is similar to the salts of tetrazole-5-carboxamidoxime (C1–C2: 1.474(3) Å; N6–C2: 1.290(3) Å; N5–C2: 1.362(2) Å; O1–N6: 1.421(2) Å; values of the ammonium salt),[113] the addition product of the aforementioned 2*H*-tetrazole-5-carbonitrile

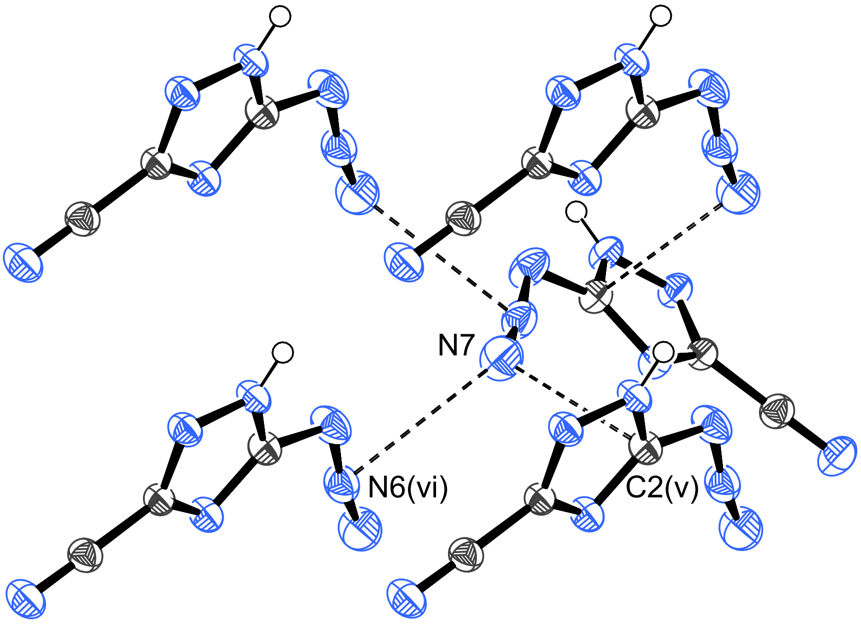


Figure 3.3: Short contacts present in 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**), showing the orientation of the two layer types. Thermal ellipsoids at 50 % probability. Symmetry codes: (v) $-x+0.5, y+0.5, -z+0.5$; (vi) $-x+1.5, y+0.5, -z+0.5$

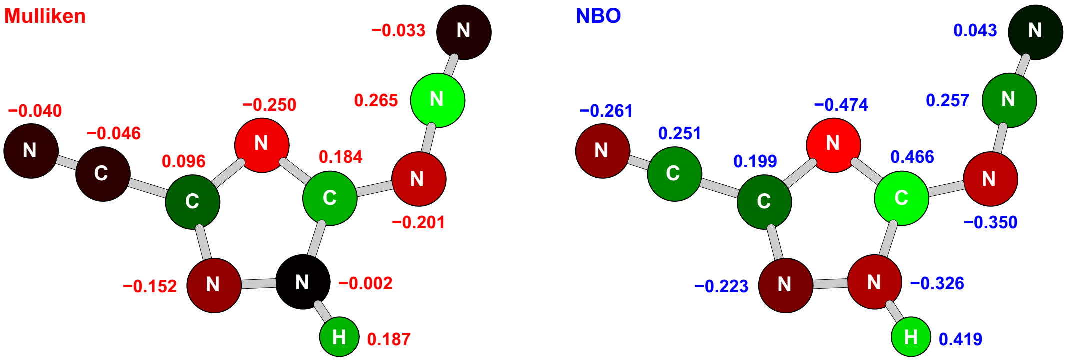


Figure 3.4: Mulliken and NBO charges on 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**).

with hydroxylamine. The proton of the oxime is slightly twisted out of the plane (torsion angle C3–N7–O1–H81: −166(2)°) due to a hydrogen bond. All four protons are participating in the hydrogen bonding network (figures 3.6 and 3.7, table 3.2). The structure consists of stacked layers of parallel chains, whereby the running direction of the layers is alternating. First, the molecules are forming twisted, parallel chains along the *c* axis, involving the ring proton and one from the amide (figure 3.6). The other proton of the amide is linking the parallel chains trough a very weak electrostatic hydrogen bond, with the terminal nitrogen of the azide acting as acceptor (figure 3.7). The proton of the hydroxyl group is connecting to the anti-parallel chain along the stacking (figure 3.7), somewhat resembling a left-handed helix. Furthermore, weak C-C short contacts ($C1\cdots C3^{v}$: 3.394(3) Å; $C2\cdots C3^{vi}$: 3.363(3) Å) slightly below the sum of the van der Waals radii and involving all three carbon atoms are

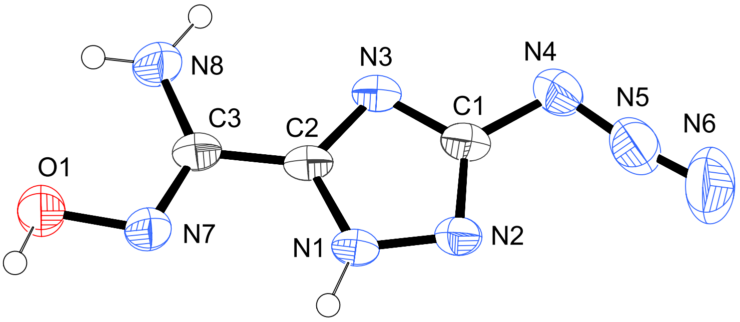


Figure 3.5: Molecular structure of 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**). Thermal ellipsoids at 50 % probability.

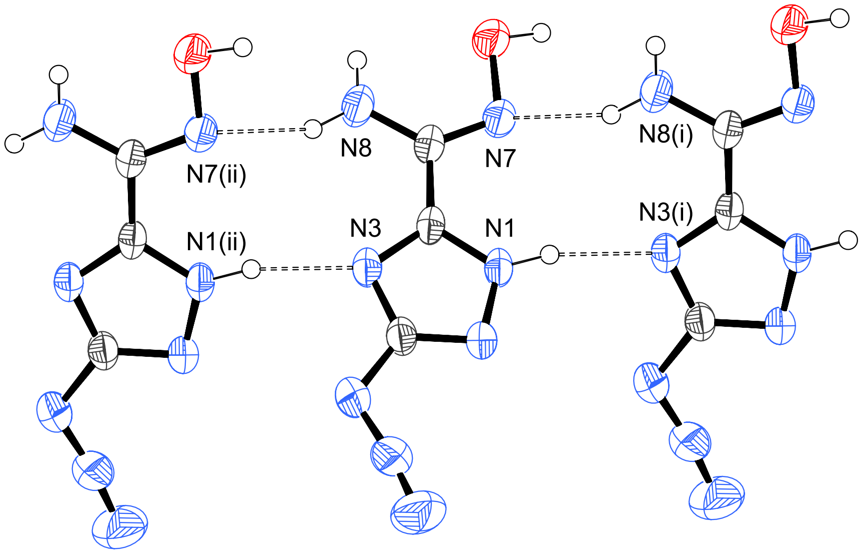


Figure 3.6: Hydrogen bonds of 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**), forming chains along the *c* axis. Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $x, -y + 0.5, z - 0.5$; (ii) $x, -y + 0.5, z + 0.5$.

connecting the molecules directly above each other along the stacking (figure 3.8).

5-Azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**) could only be obtained as an ethanol hemisolvate when recrystallized from ethanol. It crystallized in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The asymmetric unit consists of two independent molecules (the first one is shown in figure 3.9) with one ethanol molecule. Both the azide and the carbohydroximoyl chloride are rotated by 180° in comparison to the corresponding parts of **16**. The ring proton is also again relocated to the nitrogen atom next to the azide. While one of the molecules is planar (the one shown in figure 3.9) the other one displays a slight twist of the carbohydroximoyl chloride against the triazole ring by −6.8(3)° for N9–C4–C6–Cl2. The molecules are forming tilted chains along the *c* axis which are connected and stacked along the *a* axis, with the only interaction between them along the *b* axis being a N-Cl short contact ($\mathrm{Cl1 \cdots N7^{v}}$: 3.149(2) Å) below the sum of the

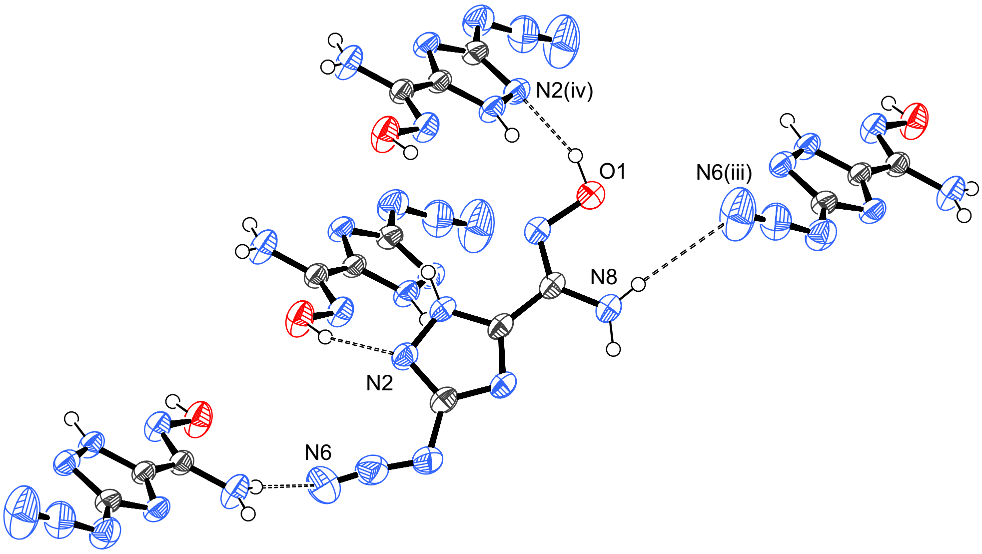


Figure 3.7: Hydrogen bonds of 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**), connecting the chains perpendicular to the c axis and in the stacking along the b axis. Thermal ellipsoids at 50 % probability. Symmetry codes: (iii) $x+1, -y+0.5, z+0.5$; (iv) $-x+1, y+0.5, -z+0.5$.

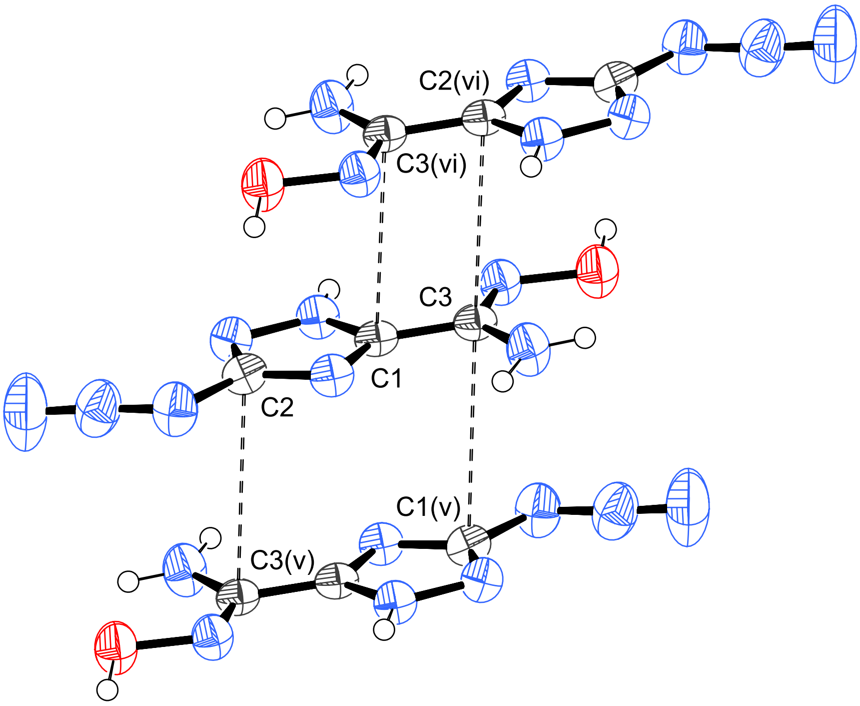


Figure 3.8: Short contacts present in 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**). Thermal ellipsoids at 50 % probability. Symmetry codes: (v) $-x+1, -y, -z+1$; (vi) $-x+1, -y+1, -z+1$.

Table 3.2: Hydrogen bonds present in 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**).

D–H$\cdots$A	d(D–H) / Å	d(H$\cdots$A) / Å	d(D$\cdots$A) / Å	$\angle$(D–H$\cdots$A) / °
N1–H71$\cdots$N3^{i}	0.90(2)	1.99(2)	2.865(2)	167(2)
N8–H781$\cdots$N7^{ii}	0.91(3)	2.22(3)	3.080(2)	156(2)
N8–H782$\cdots$N6^{iii}	0.85(2)	2.68(2)	3.527(2)	174(2)
O1–H81$\cdots$N2^{iv}	0.94(3)	2.00(3)	2.877(2)	155(3)

Symmetry codes: (i) $x, -y+0.5, z-0.5$; (ii) $x, -y+0.5, z+0.5$; (iii) $x+1, -y+0.5, z+0.5$; (iv) $-x+1, y+0.5, -z+0.5$.

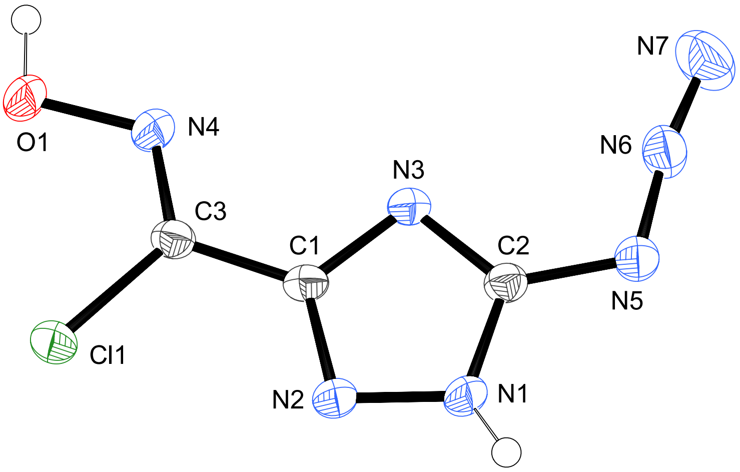


Figure 3.9: One of the two independent molecular units of 5-azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**). Thermal ellipsoids at 50 % probability.

van der Waals radii ($\sum r_w$(N,Cl) = 3.30 Å),[104] with both molecules being from the same type and again involving the terminal nitrogen atom of the azide (figure 3.11). All nitrogen and oxygen bound protons are participating in the hydrogen bonding network (table 3.3), which is illustrated in figure 3.10.

Table 3.3: Hydrogen bonds present in 5-azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**).

D–H$\cdots$A	d(D–H) / Å	d(H$\cdots$A) / Å	d(D$\cdots$A) / Å	$\angle$(D–H$\cdots$A) / °
N1–H71$\cdots$N10	0.78(2)	2.13(2)	2.902(2)	171(2)
O1–H81$\cdots$N9^{i}	0.89(2)	1.87(3)	2.748(2)	167(3)
N8–H78$\cdots$O3^{ii}	0.87(2)	1.85(3)	2.727(2)	177(3)
O2–H82$\cdots$N3^{iii}	0.81(2)	2.07(2)	2.870(2)	171(3)
O3–H83$\cdots$N2^{iv}	0.79(2)	2.21(2)	2.992(2)	170(3)

Symmetry codes: (i) $x, y, z-1$; (ii) $x, y, z+1$; (iii) $-x+1, -y+1, z+1$; (iv) $-x, -y+1, -z+1$.

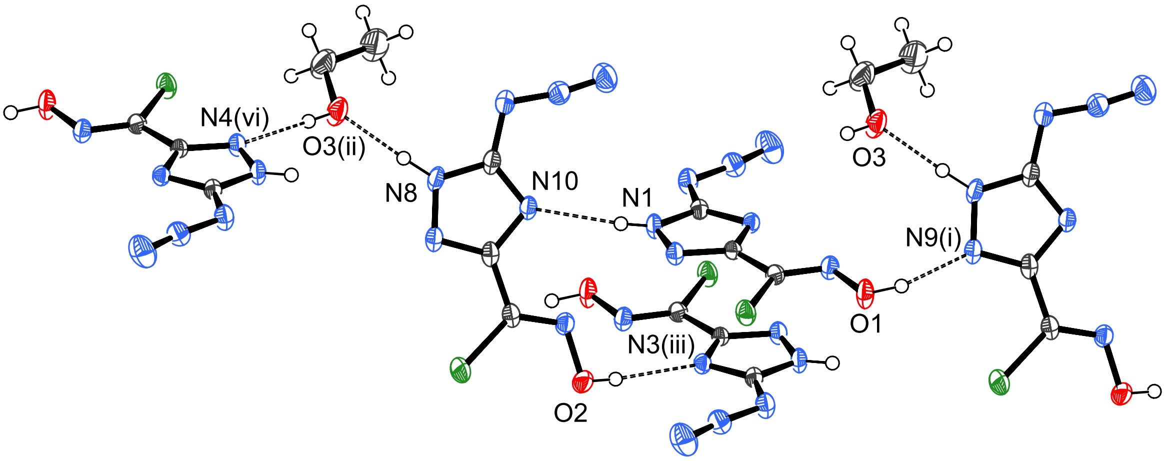


Figure 3.10: Hydrogen bonds of 5-azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**). Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $x, y, z-1$; (ii) $x, y, z+1$; (iii) $-x+1, -y+1, z+1$; (iv) $-x, -y+1, -z+1$.

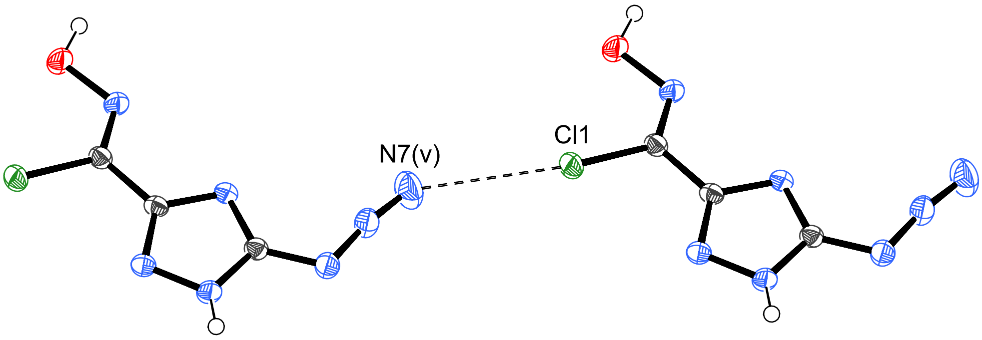


Figure 3.11: The main short contact present in 5-azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**). Thermal ellipsoids at 50 % probability. Symmetry code: (v) $x-1, y+1, z$.

3.2.3 Further Characterization

All three neutral compounds show the signal of the azide beta nitrogen atom (**15**: −140 ppm; **16**: −133 ppm; **17**: −137 ppm) in the corresponding ^{14}N NMR spectrum. The stretching mode of the terminal azide bond is visible as a strong to very strong band (**15**: 2148 cm^{-1}; **18**: 2167 cm^{-1}; **16**: 2138 cm^{-1}; **19**: 2140 cm^{-1}; **17**: 2151 cm^{-1}) in the IR spectra. While the parent compound **15** displays a rather low decomposition temperature of 161 °C, after a discrete melting point at 114 °C, its silver salt **18** is stable until 171 °C. Although the amidoxime **16** is less thermally stable with a decomposition onset of 158 °C, its silver salt **19** is slightly more thermally stable, with decomposition beginning at 166 °C. The chloro compound **17** exhibits the highest thermal stability of the three investigated neutral compounds (168 °C).

Due to the energetic *C*-azido-1,2,4-triazole backbone of **15** and **16** the enthalpies of formation were calculated at the CBS-4M level of theory and are as expected highly

Table 3.4: Energetic properties of 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) and its derivatives **16**–**19**.

Compound	IS / J	FS / N	ESD / mJ	T_d / °C	DDT	fast heating
15	25	160	500	161	—	—
16	10	240	—	158	—	—
17	6	240	—	168	—	—
18	2	16	18	171	yes	deflagration
19	3	24	10	166	no	deflagration

endothermic (**15**: 614 kJ mol^{-1}; **16**: 433 kJ mol^{-1}).

Furthermore, the sensitivities of **15**–**17** to impact and friction were determined according to BAM standards. According to the UN recommendations on the transport of dangerous goods, all neutral compounds have to be classified as sensitive to both impact (**15**: 25 J; **16**: 10 J; **17**: 6 J) and friction (**15**: 160 N; **18**: 240 N; **16**: 240 N). The silver salts are very sensitive to both impact (**18**: 2 J; **19**: 3 J) and friction (**18**: 16 N; **19**: 24 N).

3.2.4 Energetic Properties

The silver compounds were both tested for their capability of being primary explosives. A small amount (approx. 5 mg) of **18** or **19** was therefore heated on a spatula by a lighter, without direct flame contact. While compound **18** detonated upon ignition, **19** only deflagrated. Next, a small amount (again approx. 5 mg) of **18** or **19** was taped to a metal surface with transparent sticky tape and poked with a hot needle. Both **18** and **19** only deflagrated, similar to a direct flame contact. The neutral compounds **15** and **16** are therefore probably not suited as anions for novel environmentally friendly ionic primary explosives. The reason is the fact that if the silver salt of an azole shows a slow DDT (or none at all) then the other salts, for example with potassium or copper, will usually show an even lower performance.

3.3 Conclusions

The goal of the present study has been the preparation and characterization of the novel compound 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**). Its capability to form salts was demonstrated with the silver salt **18**, incorporating the novel binary C-N anion of the title compound. The reactivity of the nitrile was shown by the reaction with hydroxylamine, furnishing 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**). Compound **16** is also forming a silver salt (**19**), and the amine was successfully exchanged with a chloride when diazotated in hydrochloric acid, forming 5-azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**). All three neutral compounds (**15**, **16**, **17**) were investigated by single crystal X-ray diffraction, which revealed interesting structural motifs. While the neutral compounds are sensitive to both impact and friction, the two silver salts are very sensitive. Compounds **18** and **19** were therefore tested for being potentially primary explosives, but although **15** and **16** show high calculated enthalpies of formation, the silver salts are no ideal primary explosives due to their slow DDT.

3.4 Experimental Part

3-Amino-1*H*-1,2,4-triazole-5-carboxamide (13)

Thionyl chloride (48 mL, 0.65 mol) was added drop wise to a suspension of 3-amino-1*H*-1,2,4-triazole-5-carboxylic acid hemihydrate (68.5 g, 500 mmol) in ethanol (500 mL) at 0 °C, then refluxed for one hour. The solvent was evaporated under reduced pressure and the resulting yellow oil was treated with a concentrated solution of sodium acetate (180 g) in water (500 mL). The colorless precipitate was filtered off and washed with water, then stirred for two hours in ammonia solution (25 %, 450 mL) at 60 °C. Upon cooling down, colorless crystals were obtained (38.2 g, 301 mol, 60 %) and washed with ethanol. ^{1}H NMR (DMSO-d_6): δ = 12.38 (s, 1H, NH), 7.30 (s, 2H, NH_2), 6.10 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ = 161.6, 157.0, 154.7. IR (ATR): $\tilde{\nu}$ = 3330 (s), 3132 (s), 2243 (w), 1687 (vs), 1648 (vs), 1580 (s), 1513 (m), 1484 (vs), 1415 (s), 11354 (m), 1299 (s), 1129 (w), 1067 (s), 1010 (w), 790 (w), 729 (w), 690 (m) cm^{-1}. EA ($C_3H_5N_5O$): calculated C 28.35, H 3.97, N 55.10 %; found C 28.45, H 3.79, N 54.93 %.

5-Amino-1*H*-1,2,4-triazole-3-carbonitrile (14)

A suspension of **13** (10.0 g, 78.7 mmol) and phosphorous pentoxide (60.0 g, 423 mmol) was stirred in acetonitrile (1.2 L) for three days at room temperature. Water (200 mL) was added afterwards and stirred for further three hours. The acetonitrile was evaporated under reduced pressure and additional water (100 mL) was added to the residue, which was then extracted with ethyl acetate (3 × 150 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The solid residue was washed with *n*-pentane to yield a colorless powder (5.04 g, 46.2 mmol, 59 %). ^{1}H NMR (DMSO-d_6): δ = 13.07 (s, 1H, NH), 6.63 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ = 157.6, 135.8, 113.9. IR (ATR): $\tilde{\nu}$ = 3441 (m), 3288 (s), 3161 (s), 2256 (m), 1643 (vs), 1572 (vs), 1491 (s), 1452 (m), 1366 (s), 1315 (m), 1130 (m), 1108 (w), 1055 (vs), 1020 (m), 777 (w), 715 (vs), 656 (m) cm^{-1}. MS (DEI+): m/z = 109.2 ([M]$^+$). EA ($C_3H_3N_5$): calculated C 33.03, H 2.77, N 64.20 %; found C 33.11, H 2.82, N 62.47 %.

5-Azido-1*H*-1,2,4-triazole-3-carbonitrile (15)

Sodium nitrite (1.57 g, 22.8 mmol) was added in small portions to **14** (2.26 g, 20.7 mmol) in sulfuric acid (20 %, 125 mL) while maintaining the temperature around 5 °C. The mixture was stirred for 30 minutes, after which a small amount urea was added, followed by sodium azide (1.61 g, 24.8 mmol) in small portions. The resulting solution was stirred without cooling for one hour, then extracted with ethyl acetate (3 × 75 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The solid residue was washed with *n*-pentane to yield a colorless powder (2.43 g, 18.0 mmol, 87 %). ^{13}C NMR (DMSO-d_6): $\delta = 152.7$ (C2), 136.2 (C1), 112.1 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -140$ (N6). IR (ATR): $\tilde{\nu} = 3252$ (vs), 2497 (w), 2375 (w), 2260 (w), 2235 (w), 2200 (w), 2148 (s), 1703 (w), 1531 (vs), 1466 (m), 1454 (s), 1422 (s), 1352 (s), 1295 (s), 1191 (vs), 1132 (s), 1061 (m), 1049 (s), 1006 (m), 823 (w), 804 (s), 773 (vs), 730 (vs), 687 (s) cm^{-1}. MS (DEI+): $m/z = 135.2$ ([M]$^+$). EA (C_2HN_7): calculated C 26.67, H 0.75, N 72.58 %; found C 26.20, H 1.10, N 68.57 %. DSC (5 °C min^{-1}): $T_\mathrm{m} = 114$ °C, $T_\mathrm{d} = 161$ °C. Sensitivities (grain size < 100 µm): IS 25 J, FS 160 N, ESD 500 mJ.

3-Azido-1*H*-1,2,4-triazole-5-carboxamidoxime (16)

Hydroxylamine hydrate (50 %, 490 mg, 7.42 mmol) was added to **15** (1.00 g, 7.40 mmol) in isopropanol (20 mL) and the mixture was refluxed for 30 minutes, then cooled and stored overnight in a fridge at 4 °C. The precipitate was filtered off, washed with a small amount of isopropanol and dried at 102 °C to yield a colorless powder (772 mg, 4.59 mmol, 62 %). ^{1}H NMR (DMSO-d_6): $\delta = 14.31$ (br, NH), 10.13 (s, 1H, OH), 5.91 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 156.9$ (C2), 150.3 (C1), 142.9 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -133$ (N5). IR (ATR): $\tilde{\nu} = 3468$ (m), 3318 (m), 3295 (m), 3143 (m), 3059 (w), 2956 (m), 2881 (m), 2815 (m), 2696 (m), 2430 (w), 2380 (w), 2286 (w), 2246 (w), 2187 (w), 2138 (vs), 1661 (s), 1599 (m), 1580 (m), 1507 (w), 1492 (vs), 1472 (m), 1432 (vs), 1406 (vs), 1332 (vs), 1266 (m), 1220 (s), 1162 (m), 1097 (w), 1045 (s), 1023 (m), 948 (vs), 853 (m), 799 (s), 752 (m), 714 (w), 665 (w) cm^{-1}. MS (DEI+): $m/z = 167.1$ ([M+H]$^+$). EA ($C_3H_4N_8O$): calculated C 21.43, H 2.40, N 66.65 %; found C 21.69, H 2.45, N 65.31 %. DSC (5 °C min^{-1}): $T_\mathrm{d} = 158$ °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 240 N.

5-Azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (17)

Hydroxylamine hydrate (50 %, 1.14 g, 17.2 mmol) was added to **15** (2.30 g, 17.0 mmol) in warm water (10 mL) and the mixture was refluxed for one hour, then cooled to room temperature. It was acidified with hydrochloric acid (37 %, 10 mL) and cooled with an ice bath while sodium nitrite (2.35 g, 34.0 mmol) in water (5 mL) was carefully added drop wise under vigorous stirring. After the addition was complete the resulting suspension was stirred for two hours at room temperature. The precipitate was filtered off, washed multiple times with the mother liquor and a small amount of water, then dried at 102 °C to yield a colorless powder (2.77 g, 14.8 mmol, 87 %). ^{1}H NMR (DMSO-d_6): δ = 12.97 (OH). ^{13}C NMR (DMSO-d_6): δ = 155.9 (C1), 150.3 (C2), 126.4 (C3). ^{14}N NMR (DMSO-d_6): δ = –137 (N6). IR (ATR): $\tilde{\nu}$ = 3163 (w), 3124 (w), 3009 (w), 2929 (w), 2859 (w), 2826 (w), 2372 (w), 2267 (w), 2227 (w), 2151 (s), 1620 (w), 1549 (s), 1523 (m), 1474 (m), 1438 (m), 1395 (m), 1313 (w), 1188 (vs), 1153 (m), 1077 (m), 1043 (m), 1037 (m), 1018 (vs), 937 (vs), 768 (w), 743 (w), 729 (w), 679 (w), 664 (w) cm^{-1}. MS (DEI+): m/z = 187.1 ([M]$^{+}$). EA ($C_3H_2ClN_7O$): calculated C 19.21, H 1.07, Cl 18.90, N 52.28 %; found C 19.37, H 1.16, Cl 18.77, N 51.54 %. DSC (5 °C min^{-1}): T_d = 168 °C. Sensitivities (grain size < 100 µm): IS 6 J, FS 240 N.

Silver 5-azido-1,2,4-triazolate-3-carbonitrile (18)

Silver nitrate (340 mg, 2.00 mmol) in water (20 mL) was added drop wise to **15** (270 mg, 2.00 mmol) in water (40 mL) at 65 °C and the resulting suspension was stirred in the dark for 15 minutes. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a colorless powder (457 mg, 1.96 mmol, 98 %). IR (ATR): $\tilde{\nu}$ = 2400 (w), 2294 (w), 2269 (m), 2234 (w), 2167 (s), 2150 (m), 1478 (vs), 1470 (vs), 1442 (vs), 1429 (s), 1392 (m), 1331 (m), 1211 (s), 1107 (m), 1029 (w), 820 (w), 727 (s) cm^{-1}. EA (C_3AgN_7): calculated C 14.89, N 40.52 %; found C 15.23, N 39.97 %. DSC (5 °C min^{-1}): T_d = 171 °C. Sensitivities (grain size < 100 µm): IS 2 J, FS 16 N, ESD 18 mJ.

Silver 3-azido-1,2,4-triazolate-5-carboxamidoxime (19)

Silver nitrate (170 mg, 1.00 mmol) in water (10 mL) was added drop wise to **16** (168 mg, 1.00 mmol) in water (20 mL) at 65 °C and the resulting suspension was stirred in the dark for 15 minutes. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a colorless powder (260 mg, 946 µmol, 95 %). IR (ATR): $\tilde{\nu}$ = 3474 (w), 3358 (w), 3147 (w), 3083 (w), 2850 (m), 2431 (w), 2303 (w), 2140 (vs), 1657 (m), 1585 (w), 1530 (w), 1481 (vs), 1286 (m), 1220 (s), 1099 (w), 1048 (w), 947 (s), 836 (w), 803 (w), 775 (m), 748 (w), 710 (m) cm^{-1}. EA ($C_3H_3AgN_8O$): calculated C 13.10, H 1.10, N 40.75 %; found C 13.41, H 1.28, N 40.27 %. DSC (5 °C min^{-1}): T_d = 166 °C. Sensitivities (grain size < 100 µm): IS 3 J, FS 24 N, ESD 10 mJ.

5-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol

A. A. Dippold, D. Izsák, T. M. Klapötke
Chem. Eur. J. **2013**, *19*, 12042–12051

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Eur. J. Inorg. Chem. **2013**, 5641–5651

4.1 Introduction

An interesting approach for energetic materials design is the formation of bisazole compounds either with a C–C bond, for example as employed for imidazole,[129,130] 1,2,4-triazole,[131,132] and tetrazole,[133–137] or mixed compounds like 5-(3-azido-1,2,5-oxadiazol-4-yl)tetrazol-1-ol,[138] and 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)-2*H*-tetrazole,[139] or with a C–N bond like 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**),[140–142] or using an azo bridge, for example in 4,4′-azoxybis(3-amino-1,2,5-oxadiazole),[143,144] or 5,5′-azobis(tetrazole).[145–147] Combination of two different heterocycles can be beneficial due to the vast possibilities of tailoring the energetic performances.

The C-C linkage of 3- or 5-substituted 1,2,4-triazoles, for example, with a tetrazole moiety benefits from the energetic tetrazole ring, the higher stability of the triazole ring and the second carbon atom of the triazole which can be further substituted with various energetic groups. Furthermore, in this case both rings carry an acidic nitrogen-bound proton each, thus enabling the formation of energetic salts by Brønsted acid-base and/or salt metathesis reactions.

The introduction of hydroxyl groups and *N*-oxides has recently been reintroduced as a method to raise the densities of the corresponding compounds for an even greater energy output.[148,149] One method for achieving this, is the oxidation of the nitrogen-rich heterocycles with oxidizing agents like trifluoroperacetic acid,[150] potassium peroxomonosulfate (Oxone®),[149,151] or hypofluorous acid.[152] The often low selectivity and high oxidation potential of those compounds can lead to several isomers or even a complete decomposition of the starting material, especially in the case of compounds with several oxidizable nitrogen atoms. An alternative route is the introduction of the oxygen atom during the synthesis of the tetrazole ring instead of subsequent oxidation, leading exclusively to 1-hydroxytetrazoles.[136–138]

As was shown in chapters 2 and 3, both 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) and 5-

azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) are able to form primary explosives, yet the resulting salts exhibit mostly only marginally better thermal stabilities than the neutral compounds. A possible solution to this problem could be the introduction of a second nitrogen-rich heterocycle, preferably a tetrazole, as second energetic group. Tetrazoles have the tendency that deprotonation and salt formation usually raises the thermal stability,[153] but not necessarily the mechanical stability which would be greatly beneficial for primary explosives.[28,29]

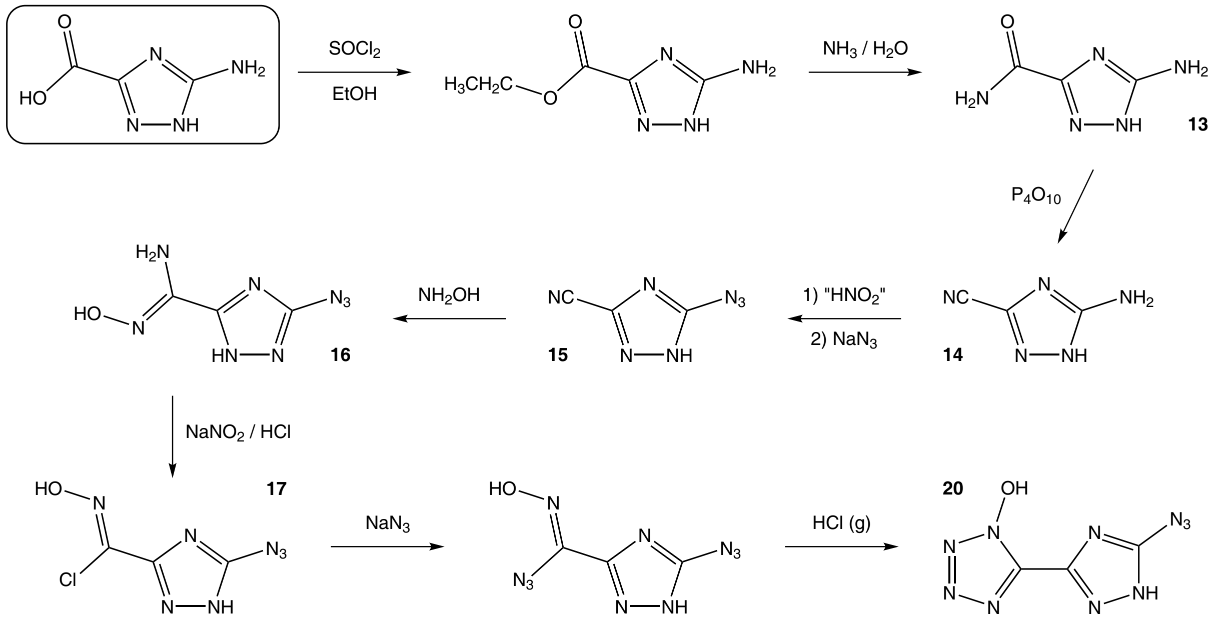
Thus, the goal of this study has been the preparation of the novel compound 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) and its salts (1:1 and 2:1) with several metal and nitrogen-rich cations to investigate the effects of deprotonation on the thermal and mechanical stabilities of the resulting salts as well as the applicability of the metal salts as primary explosives.

4.2 Results and Discussion

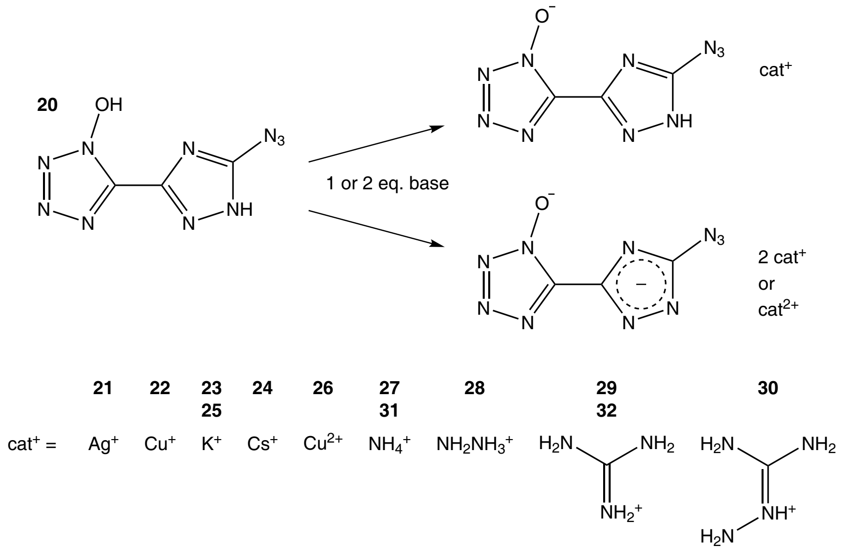
4.2.1 Syntheses

The parent compound 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) was synthesized by a multi-step method as illustrated in scheme 4.1, starting from commercially available 3-amino-1*H*-1,2,4-triazole-5-carboxylic acid via the previously investigated intermediate 5-azido-1*H*-1,2,4-triazole-3-carbohydroxymoyl chloride (**17**), in a similar way as previously reported methods.[136,137] It is not necessary to isolate the carbohydroxymoyl azide intermediate, which was, in turn, obtained by the reaction of **17** with sodium azide in ethanol, before the final ring closure with hydrogen chloride gas in diethyl ether.

The alkali metal salts with potassium (**23**, **25**) and cesium (**24**), as well as the nitrogen-rich salts with ammonium (**27**, **31**), hydrazinium (**28**), guanidinium (**29**, **32**) and aminoguanidinium (**30**) were prepared according to scheme 4.2 in ethanolic solution using **20** and the corresponding carbonates, hydrogen carbonates, or free bases and subsequent precipitation of the salt or evaporation of the solvent under reduced pressure. The silver salt **21** was prepared by the reaction of the neutral compound with silver nitrate in water. The copper(I) salt **22** was prepared according to the preparation of DBX-1 by the reaction of the in situ prepared sodium salt of **20** with copper(II) chloride in water and the subsequent reduction of copper(II) to copper(I) using sodium ascorbate.[28] The copper(II) salt **26** was prepared by the reaction of copper(II) chloride with the in situ prepared sodium salt of **20** in water.



Scheme 4.1: Synthetic route towards 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) from commercially available 3-amino-1H-1,2,4-triazole-5-carboxylic acid.



Scheme 4.2: Synthesis of the salts **21**–**32** with single and two times deprotonated 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**).

4.2.2 Crystal Structure Analysis

5-(5-Azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) crystallized as monohydrate in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The molecule shows a nearly planar assembly with a torsion angle between the two heterocycles of 2.9(2)°. The azido group is slightly twisted out of the triazole plane by −7.3(2)°. The proton is located at the nitrogen atom next to the C-N bond, in contrast to the nitro derivative NTTO.[154] The

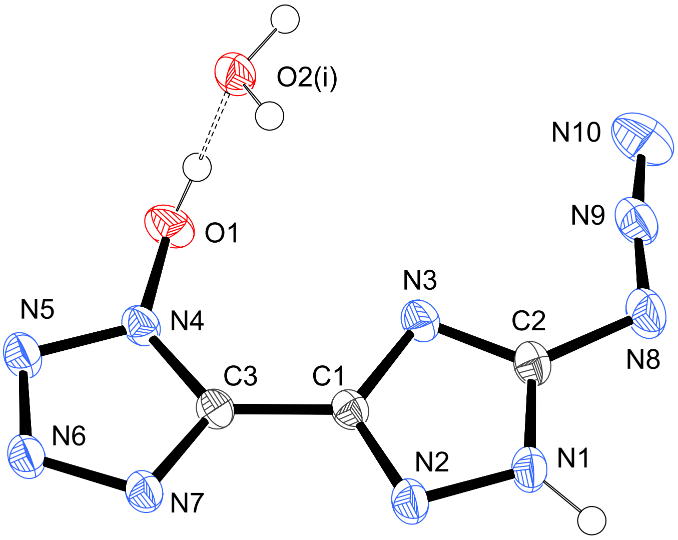


Figure 4.1: Molecular structure of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**). Thermal ellipsoids at 50 % probability. Symmetry code: (i) $x, y, z+1$.

Table 4.1: Hydrogen bonds present in 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**).

D–H···A	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	∠(D–H···A) / °
N1–H1···O2	0.91(2)	2.07(2)	2.824(2)	140(2)
N1–H1···N2^{ii}	0.91(2)	2.51(2)	3.175(2)	130(2)
O1–H1O···O2^{i}	0.97(3)	1.61(3)	2.574(2)	175(3)
O2–H2A···N7^{ii}	0.87(2)	1.94(2)	2.805(2)	170(2)
O2–H2B···N6^{v}	0.85(2)	1.99(2)	2.838(2)	177(2)

Symmetry codes: (i) $x, y, z+1$; (ii) $-x, -y+1, -z+1$; (v) $x, y-1, z-1$.

formula unit of **20** together with the atom labeling is presented in figure 4.1. The molecules are forming dimers between two triazole rings with a very weak and mostly electrostatic N1–H1···N2^{ii} hydrogen bond (N1···N2^{ii}: 3.175(2) Å). This is similar to the precursor **15**, but there the bond is much stronger (N1···N2^{i}: 2.993(2) Å). The dimers in turn are forming endless parallel chains utilizing the water molecule and with N6 and N7 of the tetrazole ring acting as additional acceptors. The connection between the chains is established by a directed $N_\gamma \cdots O$ interaction between the terminal nitrogen atom of the azide and the hydroxyl group (N10···O1^{iv}: 2.879(2) Å; N9–N10···O1^{v}: 166.7(1)°) well below the sum of the van der Waals radii ($\sum r_w$(N,O) = 3.07 Å).[104] The primary hydrogen bonding network and the short contact are illustrated in figure 4.2 and the parameters are compiled in table 4.1. Finally, the planes are connected by a strong hydrogen bond O1–H1O···O2^{i} between the hydroxyl proton and the water molecule.

Potassium 5-(3-azido-1,2,4-triazol-5-yl)tetrazol-1-olate (**23**) crystallized as a monohydrate in the triclinic space group $P\bar{1}$. The molecular unit is depicted in figure 4.3. The hydroxyl

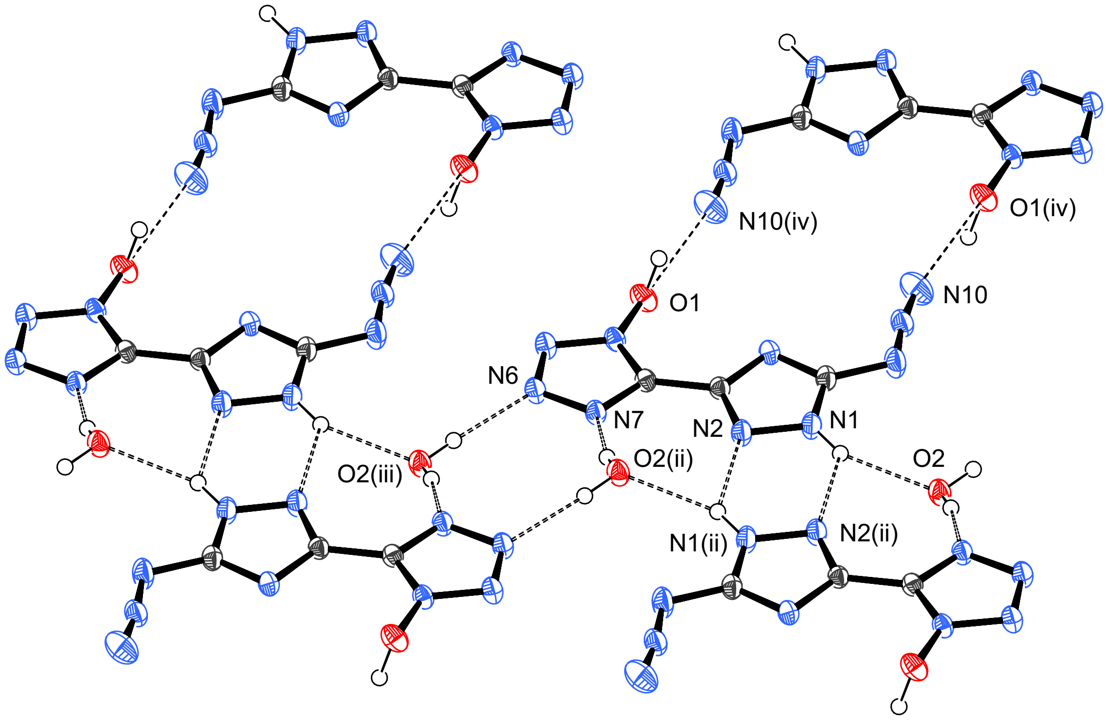


Figure 4.2: Formation of planes in the crystal structure of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**), made up from infinite parallel chains. Thermal ellipsoids at 50 % probability. Symmetry codes: (ii) $-x, -y+1, -z+1$; (iii) $x, y+1, z+1$; (iv) $-x+1, -y, -z+2$.

group is more acidic than the triazole ring with the former being deprotonated first, but interestingly the proton of the latter (H1) is relocated to the nitrogen atom neighboring the C-C bond. In contrast to the parent compound **20** the tetrazol-1-olate is rotated by 180°. The compound is the only one in this study in which the azide is also rotated by 180°, resembling the structure of the precursor 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**). The deprotonation of the hydroxyl group is only marginally affecting the bond lengths and angles of the tetrazole ring. The triazole ring is similar to the aforementioned precursor. The structure features an interesting cation-water-framework, similar to **25** $\cdot$ 3 H_2O (see later on). The asymmetric unit consists of a $[K_2(H_2O)_2]^{2+}$ unit, with K1$\cdots$O2 (3.080(1) Å) and K1$\cdots$O2^{i} (2.800(1) Å) contacts. These rhombi (O2$\cdots$K1$\cdots$O2^{i}: 103.75(3)°) are connected by a K1$\cdots$O2^{ii} (2.804(1) Å) contact, forming an almost perfect square (O2$^{i}\cdots$K1$\cdots$O2^{ii}: 89.81(4)°) and a wave-pattern of the band (O2$\cdots$K$\cdots$O2^{ii}: 137.73(3)°). The framework is illustrated in figure 4.4. The structure further contains a total of four hydrogen bonds stemming from the three hydrogen atoms, whereby H1 is involved in two of them. Very striking are the dimers of AzTTO^{-} anions, connected by a N1–H1$\cdots$N2^{iv} contact (D$\cdots$A: 2.933(2) Å; D–H$\cdots$A: 137(2)°) below the sum of the van der Waals radii ($\sum r_{w}$(N,N) = 3.10 Å).[104] This is similar to **20** (D$\cdots$A: 3.175(2) Å; D–H$\cdots$A: 130(2)°) and the precursor **15** (D$\cdots$A: 2.993(2) Å; D–H$\cdots$A: 126(1)°). Additionally H1 is involved in a second,

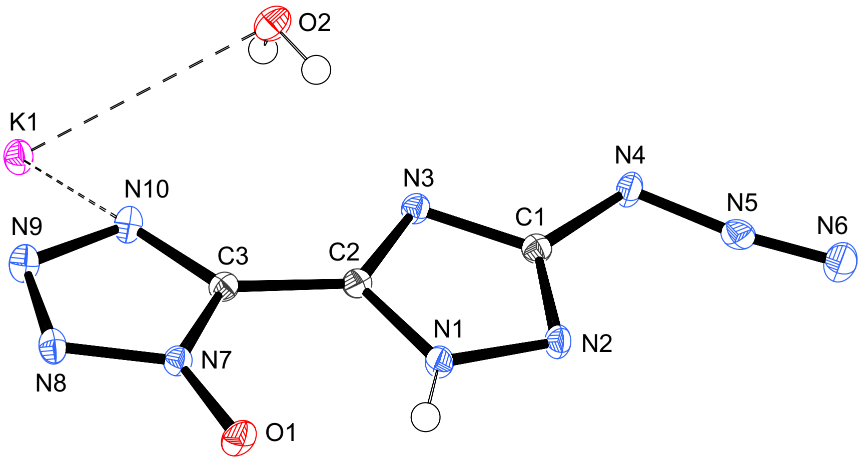


Figure 4.3: Molecular structure of potassium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate monohydrate (**23** · H_2O). Thermal ellipsoids at 50 % probability.

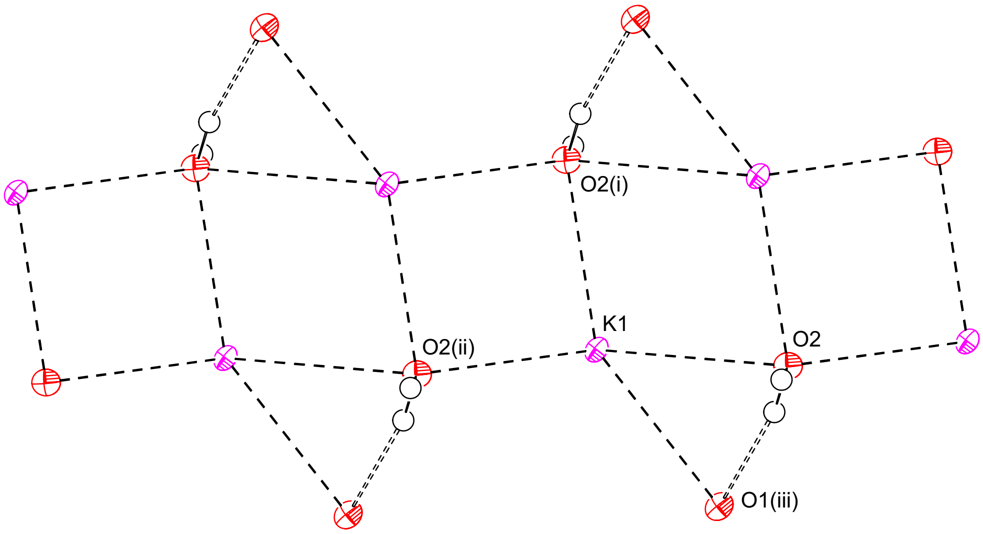


Figure 4.4: Part of the $\{[K_2(H_2O)_2]^{2+}\}_\infty$ backbone of potassium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate monohydrate (**23** · H_2O). Hydrogen atoms are partially omitted for clarity. Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, y, z$; (iii) $x, y+1, z$.

intramolecular, hydrogen bond N1–H1···O1 (D···A: 2.726(2) Å; D–H···A: 121(2)°) with the tetrazole ring, being well below the sum of the van der Waals radii ($\sum r_\mathrm{w}$(N,O) = 3.07 Å),[104] which can explain the relocation of H1 on the triazole ring. The other two hydrogen bonds both involve the water molecule, with one of the bonds (O2–H2B···$O1^{iii}$) having again O1 as acceptor and thus resulting in a strong (D···A: 2.770(1) Å) and very directed (D–H···A: 169(2)°) contact (see figure 4.5 and table 4.2), well below the sum of the van der Waals radii ($\sum r_\mathrm{w}$(O,O) = 3.04 Å).[104]

Cesium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate (**24**) crystallized in the monoclinic space group $P2_1/c$ and is the only compound in this study without the inclusion of crystal

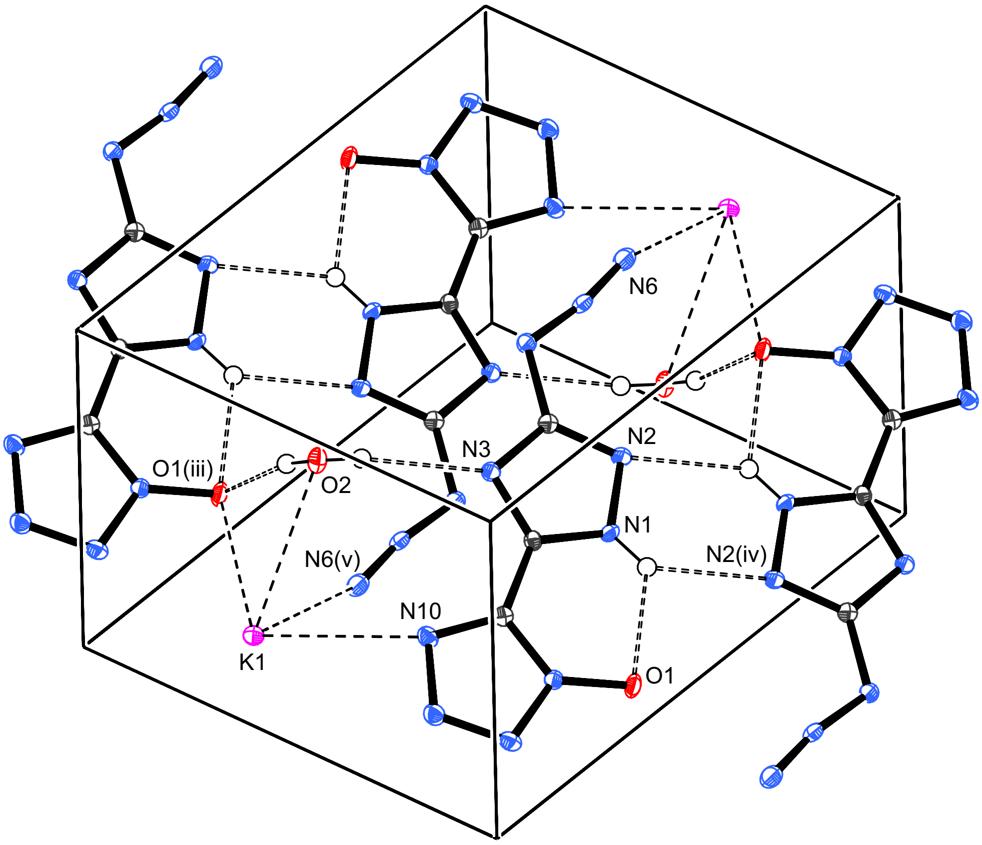


Figure 4.5: Extended unit cell of potassium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate monohydrate (**23** · H_2O), illustrating the hydrogen bonding network. Thermal ellipsoids at 50 % probability. Symmetry codes: (iii) $x, y+1, z$; (iv) $-x+1, -y, -z+1$; (v) $-x+1, -y+1, -z+1$.

Table 4.2: Hydrogen bonds present in potassium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate monohydrate (**23** · H_2O).

D–H···A	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	∠(D–H···A) / °
N1–H1···$N2^{iv}$	0.82(3)	2.28(2)	2.933(2)	137(2)
N1–H1···O1	0.82(3)	2.20(2)	2.726(2)	121(2)
O2–H2A···N3	0.76(2)	2.19(2)	2.943(2)	171(2)
O2–H2B···$O1^{iii}$	0.85(2)	1.93(2)	2.770(1)	169(2)

Symmetry codes: (iii) $x, y+1, z$; (iv) $-x+1, -y, -z+1$.

water. The molecular unit is depicted in figure 4.6. As with the potassium salt (**23** · H_2O), the proton of the triazole ring is relocated to the nitrogen atom neighboring the C-C bond. Its position had to be calculated (HFIX 43) due to a distortion of its electron density out of the ring plane into the direction of the nearby oxygen atom ($O1^{ii}$), and a too short N-H bond (N1–H1: < 0.7 Å) if refined freely. No further electron density could be observed in proximity to N2 (nor to N1), which is additionally coordinating to the cesium cation

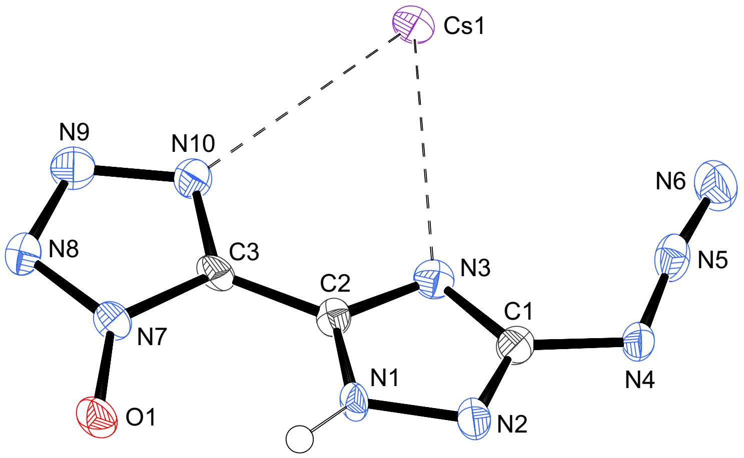


Figure 4.6: Molecular structure of cesium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate (**24**). Thermal ellipsoids at 50 % probability.

and thus confirming the correct assignment of the proton to N1. The tetrazole and the azide are virtually lying in one plane and the triazole ring is slightly tilted downwards (N3–C2–C3–N10: −9.6(9)°; N3–C1–N4–N5: 11.2(8)°). The cesium cation is also in this plane and coordinating to the nitrogen atoms N3 and N10 (Cs1–N3: 3.426(4) Å; Cs1–N10: 3.310(4) Å). A longer contact between the cesium and the terminal nitrogen atom of the azide is connecting the ion pairs (Cs1–N6^{i}: 3.626(5) Å), thus forming dimers. These dimers are linked by the only hydrogen bond of the structure, with the oxygen acting as acceptor (N1–H1: 0.880(4) Å; H1$\cdots$O1^{ii}: 2.080(4) Å; N1$\cdots$O1^{ii}: 2.743(6) Å; N1–H1$\cdots$O1^{ii}: 131.5(3)°). Although the bond is quite undirected due to the missing flexibility of the N1–H1 bond it is still rather strong due the O-N distance being well below the sum of the van der Waals radii. This special positioning of the oxygen and the nitrogen atoms is probably the reason for the aforementioned distortion of the proton's electron density (additionally to the heavy atom cesium) out of the ring plane and directed towards the oxygen. The resulting connection is depicted in figure 4.7. The strands are connected through the cesium cations and show various running directions, but the ring-systems are always parallel to each other, resulting in a sort of a multilayer structure.

Dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate (**25**) crystallized as a trihydrate in the triclinic space group $P\bar{1}$. The molecular unit is depicted in figure 4.8. The structure confirms the deprotonation of both rings, with the oxygen again pointing into the opposite direction of the azide. The main striking structural motive is the formation of a cation-water-framework, built up by the two potassium cations and all three water molecules, similar to **23** · H_2O but strongly enhanced. The asymmetric unit of the framework is the $[K_2(H_2O)_3]^{2+}$ part from the molecular unit. These are connected to a $[K_4(H_2O)_6]^{4+}$ subunit by a K2$\cdots$O2^{i} contact (2.851(1) Å) of similar length than the K2$\cdots$O3 contact

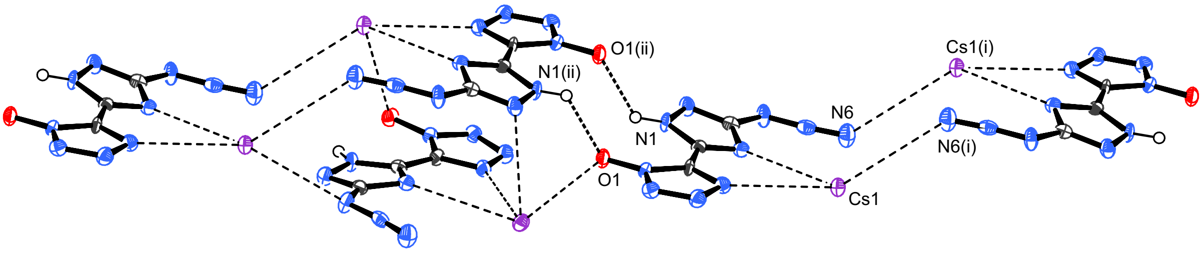


Figure 4.7: Strands in the structure of cesium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate (**24**). Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+2, -y+1, -z+1$.

(2.853(2) Å), whereby the second part is mirrored. These subunits are connected to a $\{[K_4(H_2O)_6]^{4+}\}_\infty$ band by a K2···O4^{ii} contact (2.704(2) Å), which is shorter than the K1···O4 contact (2.778(2) Å) of the molecular unit. The $[K_4(H_2O)_6]^{4+}$ subunits are further connected to a second $\{[K_4(H_2O)_6]^{4+}\}_\infty$ band perpendicular to the first $\{[K_4(H_2O)_6]^{4+}\}_\infty$ band by a K1···O3^{iii} contact (2.898(2) Å; (iii) $-x+1, -y, -z$). This structural backbone is illustrated in figure 4.9. The AzTTO^{2-} anions are docked to this backbone by coordination to the potassium cations and by rather strong and directed hydrogen bonds utilizing all water protons and with O1, N1, N3 and, surprisingly, N8 acting as acceptors (see figure 4.10 and table 4.3). Contrary to the cesium cation of **24** the potassium cations of **25** · 3 H_2O favor the coordination to N2 (N1 in **24**). As for the hydrogen bonds, all are below the sum of the van der Waals radii. Except for the O3–H3B···N3^{vii} contact, which bridges the $\{[K_2(H_2O)_3]^{2+}\}_\infty$ frameworks, all acceptors are on the same side of the anion. The two strongest hydrogen bonds O4–H4A···O1^{vi} (D···A: 2.743(2) Å) and O3–H3A···O1^{ii} (D···A: 2.775(3) Å) have both the tetrazole oxygen atom as acceptor. The weakest are O2–H2B···N1 (D···A: 2.945(3) Å) of the molecular unit and the O4–H4B···N8^{iv} (D···A: 3.047(3) Å) to the azide alpha nitrogen atom. The latter is mostly of an electrostatic nature,[105] but still plausible owing to N8 being the azide nitrogen atom with the most negative partial charge, also evidenced by the strong high-field shift in NMR spectroscopy. As pointed out earlier, the bonds are strongly directed with all angles being between 170(3) and 173(4)°. It is interesting to note that the intramolecular angle of the second water molecule (H3A–O3–H3B: 99(3)°) is slightly smaller than usually expected. This can be explained by the two hydrogen bonds and the coordination to a potassium cation. The O3–H3B···N3^{vii} contact is the most directed hydrogen bond of the structure with 173(4)° and a further approach to 180° is hardly possible due to the K1···O3–H3B angle being only 75(3)°. An enlargement of the intramolecular angle in the water molecule would therefore result in an even less directed O3–H3A···O1^{ii} angle than 170(3)°, which is less likely when thinking of the proton affinity of the tetrazole bonded oxygen atom, similar to the problem in **24**.

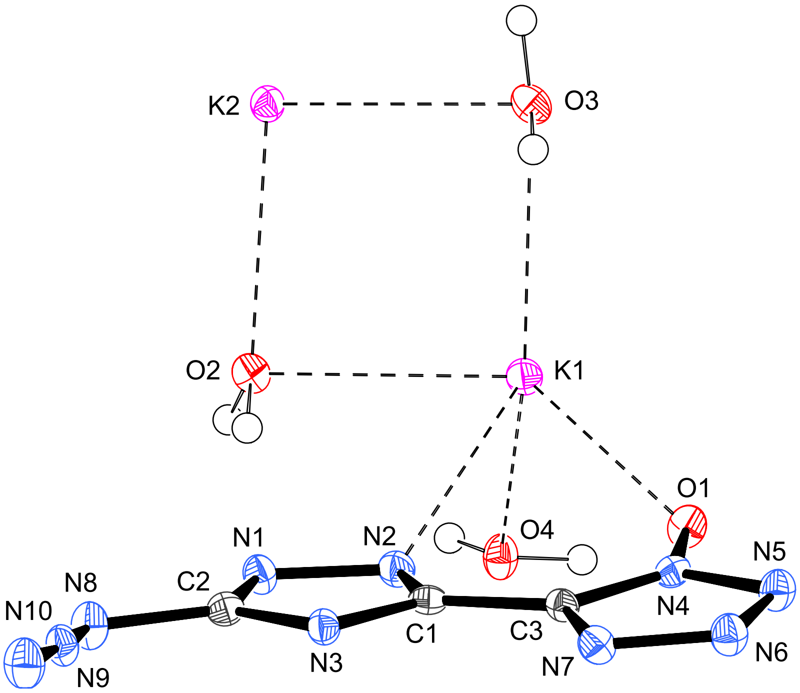


Figure 4.8: Molecular structure of dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate trihydrate ($\mathbf{25} \cdot 3\,H_2O$). Thermal ellipsoids at 50 % probability.

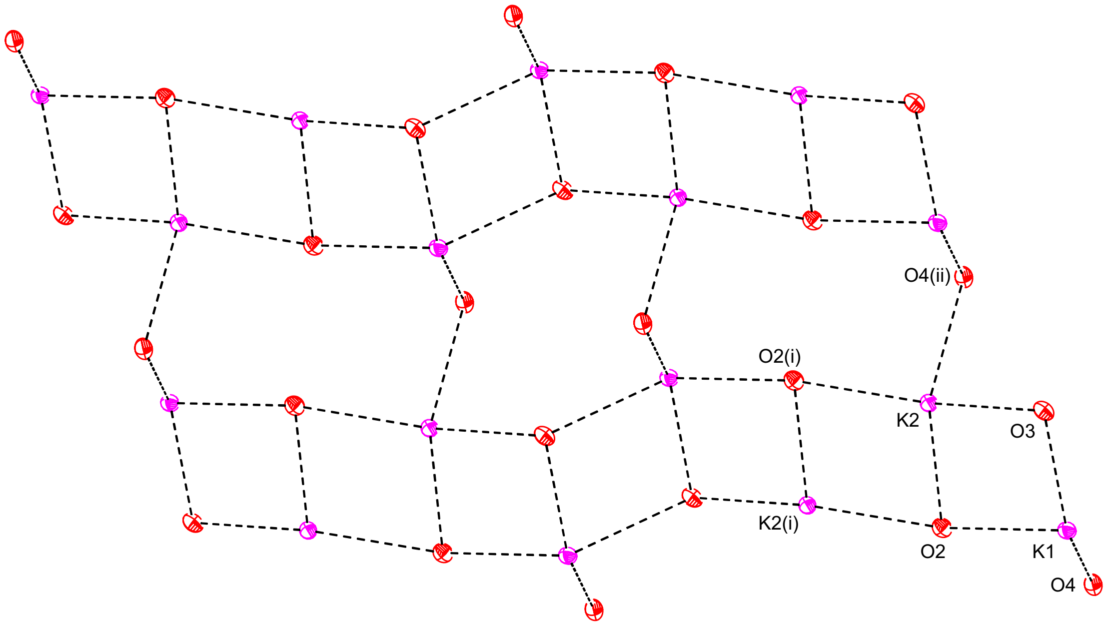


Figure 4.9: $[K_{16}(H_2O)_{32}]^{16+}$ unit of the $\{[K_4(H_2O)_6]^{4+}\}_\infty$ backbone of dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate trihydrate ($\mathbf{25} \cdot 3\,H_2O$). Hydrogen atoms are omitted for clarity. Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, y, z$.

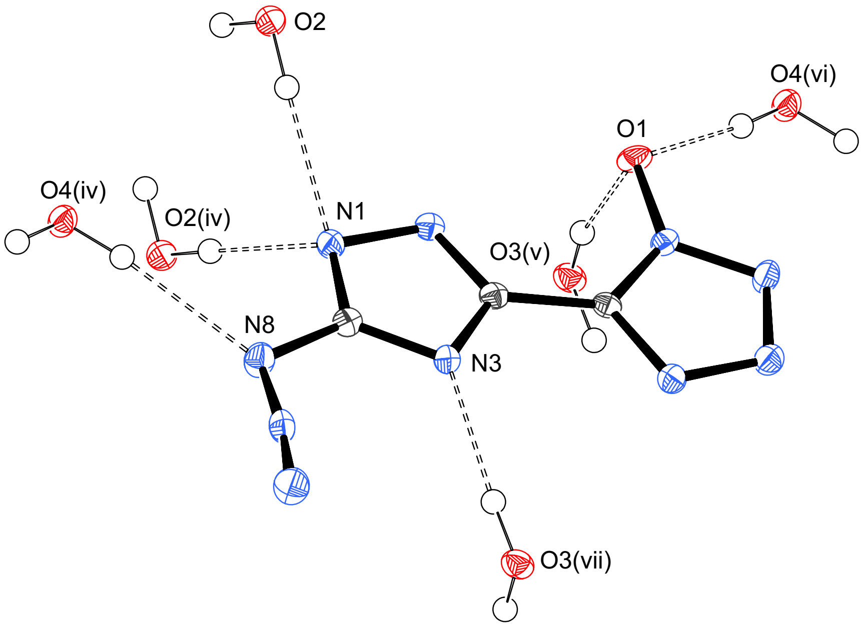


Figure 4.10: Surrounding of the AzTTO^{2-} anion in the crystal structure of dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate trihydrate (**25** $\cdot$ 3 H_2O). Thermal ellipsoids at 50 % probability. Symmetry codes: (iv) $-x+1, -y+1, -z+1$; (v) $x-1, y, z$; (vi) $-x, -y, -z$; (vii) $-x+1, -y, -z+1$.

Table 4.3: Hydrogen bonds present in dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate trihydrate (**25** $\cdot$ 3 H_2O).

D–H$\cdots$A	d(D–H) / Å	d(H$\cdots$A) / Å	d(D$\cdots$A) / Å	$\angle$(D–H$\cdots$A) / °
O2–H2A$\cdots$N1^{iv}	0.90(4)	1.94(4)	2.833(3)	170(3)
O2–H2B$\cdots$N1	0.76(3)	2.19(3)	2.945(3)	171(3)
O3–H3A$\cdots$O1^{ii}	0.85(4)	1.93(4)	2.775(3)	170(3)
O3–H3B$\cdots$N3^{vii}	0.85(5)	2.03(5)	2.876(3)	173(4)
O4–H4A$\cdots$O1^{vi}	0.83(3)	1.91(3)	2.743(2)	172(3)
O4–H4B$\cdots$N8^{iv}	0.78(4)	2.27(4)	3.047(3)	171(3)

Symmetry codes: (ii) $x+1, y, z$; (iv) $-x+1, -y+1, -z+1$; (vi) $-x, -y, -z$; (vii) $-x+1, -y, -z+1$.

Ammonium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate monohydrate (**27**) also crystallized in the triclinic space group $P\bar{1}$. The oxygen of the tetrazole ring and the azide are again pointing into opposite directions, but compared to **23** $\cdot$ H_2O and **24** the proton of the triazole ring is relocated to the nitrogen that neighbors the azide, similar to **20**. As shown in figure 4.11 each AzTTO$^-$ anion is surrounded by three ammonium cations and three water molecules, linked together by hydrogen bonds. Interestingly, although each of the six different hydrogen atoms of the ammonium cation and the water molecule participate in the hydrogen bonding network, the nitrogen atoms N2 and N3 from the triazole ring are nonparticipating. The oxygen of the tetrazole ring is acting as an acceptor for three of the

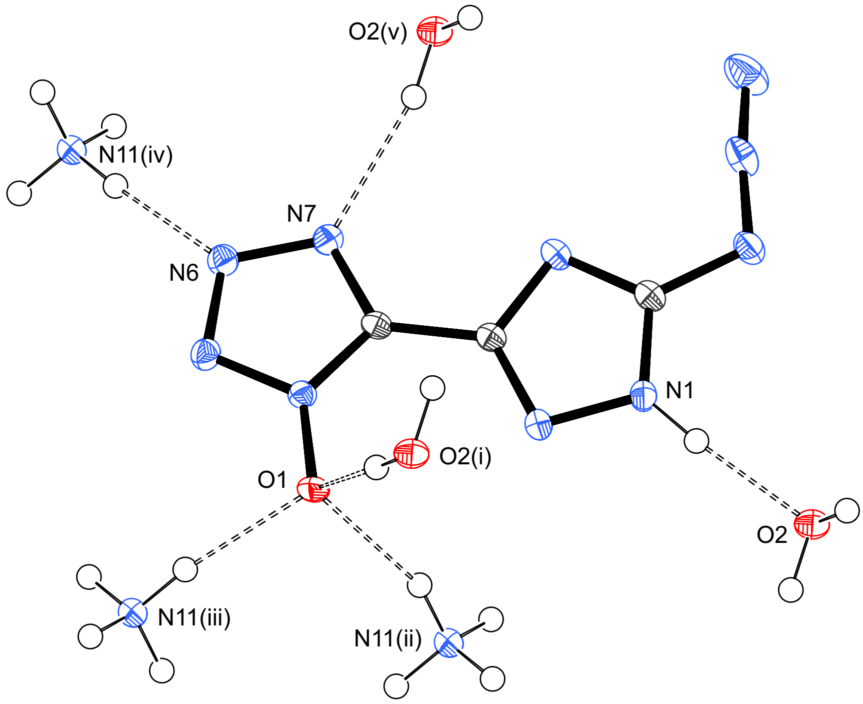


Figure 4.11: Surrounding of the AzTTO⁻ anion in the crystal structure of ammonium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate monohydrate (**27**). Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y+1, -z$; (iii) $x-1, y, z-1$; (iv) $-x+1, -y+2, -z$; (v) $x, y+1, z$.

Table 4.4: Hydrogen bonds present in ammonium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate monohydrate (**27**).

D–H· · · A	d(D–H) / Å	d(H· · · A) / Å	d(D· · · A) / Å	∠(D–H· · · A) / °
N1–H1· · · O2	0.93(3)	1.82(3)	2.741(2)	171(2)
O2–H2A· · · N7^{vi}	0.87(2)	2.11(2)	2.961(1)	166(2)
O2–H2B· · · O1^{vii}	0.93(2)	1.87(2)	2.797(2)	176(2)
N11–H11A· · · O2	0.95(2)	1.91(2)	2.861(1)	175(2)
N11–H11B· · · O1^{viii}	0.90(2)	1.96(2)	2.852(2)	171(2)
N11–H11C· · · N6^{iv}	0.92(2)	2.07(2)	2.983(2)	176(2)
N11–H11D· · · O1^{ix}	0.91(2)	2.01(2)	2.888(2)	161(2)

Symmetry codes: (iv) $-x+1, -y+2, -z$; (vi) $x, y-1, z$; (vii) $-x, -y+1, -z$; (viii) $x+1, y, z+1$; (ix) $-x+1, -y+1, -z$.

hydrogen bonds. The bonds are mostly strong and directed with D· · · A distances between 2.741(2) and 2.983(2) Å and D–H· · · A angles between 161(2) and 176(2)° (table 4.4).

From the five investigated crystal structures it can be concluded that although the hydroxyl group of neutral **20** is more acidic than the triazole ring, as shown in the three salts **23**, **24** and **27** with the mono-anion, it still exhibits a high proton-affinity, thereby resulting in (often several) rather strong and directed hydrogen bonds.

4.2.3 NMR and IR Spectroscopy

Compounds **20**, **23**, **24** and **27**–**32** were analyzed by ^{1}H, ^{13}C and ^{14}N NMR spectroscopy in DMSO-d_6. The numbering of the atoms is according to **20** itself (due to the change of numbering for **23** and **24**), with N1 being the nitrogen beside the C2-bonded azide. While **20** shows one broad signal at 9.51 ppm, the metal salts **23** and **24** show no visible signal in their corresponding ^{1}H NMR spectrum due to a fast proton exchange in DMSO. The nitrogen-rich salts **27**–**29**, **31** and **32** show only one signal between 6.41 and 7.43 ppm, also due to proton exchange. The aminoguanidinium salt **30** shows the four distinctive resonances of the cation at 8.63 (NH), 7.26 ($C{-}NH_2$), 6.83 ($C{-}NH_2$) and 4.70 ppm ($N{-}NH_2$). The effect of deprotonation only marginally affects the shifts of the three carbon atoms in the ^{13}C NMR spectra. While **20** itself displays signals at 155.2 (C2), 144.6 (C1) and 139.7 ppm (C3), the signals of the 1:1 salts **23**, **24** and **27**–**30** are at 156.5 to 157.2 ppm (C2), at 144.3 to 146.1 ppm (C1) and at 134.3 to 135.9 ppm (C3). The 2:1 salt **31** shows signals very similar to the 1:1 salt **27**, probably due to a fast proton exchange, and **32** shows signals at 155.3 (C2), 149.2 (C1) and 138.4 ppm (C3), clearly distinguishable from the 1:1 salt **29**. Compounds **29** and **32** further show the signal of the cation around 158 ppm and **30** at 158.8 ppm. The azide beta nitrogen atom is visible as a broad signal in the ^{14}N NMR spectra with a signal maximum between −132 and −137 ppm. Compounds **27** and **31** further show the sharp signal of the ammonium cation around −358 ppm. The parent compound **20** was additionally analyzed by ^{15}N NMR spectroscopy, also in DMSO-d_6 (figure 4.12). In contrast to the nitro derivative (all atoms show visible signals),[154] **20** shows only eight well resolved resonances instead of the expected ten, similar to 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**).[139] The two missing signals are the triazole nitrogen atoms N1 and N2, probably resulting from a fast proton exchange. The assignments were based on comparison with theoretical calculations (MPW1PW91/aug-cc-pVDZ). The signals of the tetrazol-1-ol are similar to 5,5′-bis(tetrazol-1-ol),[155] and found at −117.8 (N4), −18.1 (N5), −4.1 (N6) and −55.3 ppm (N7). The remaining signals are at shifts of −150.8 (N3), −295.3 (N8), −145.6 (N9) and −144.0 ppm (N10).

All compounds are easily identified by IR spectroscopy due to the characteristic asymmetric stretching mode of the azide (nitrogen atoms N9 and N10) as a sharp and mostly very strong band between 2133 and 2159 cm^{-1}.

4.2.4 Thermal Stabilities

The thermal behavior of the synthesized compounds was analyzed by differential scanning calorimetry measurements. The decomposition temperatures of the investigated salts range from 184 °C (**21**) up to 281 °C (**22**) for the metal salts and from 171 °C (**30**) to 182 °C (**29**)

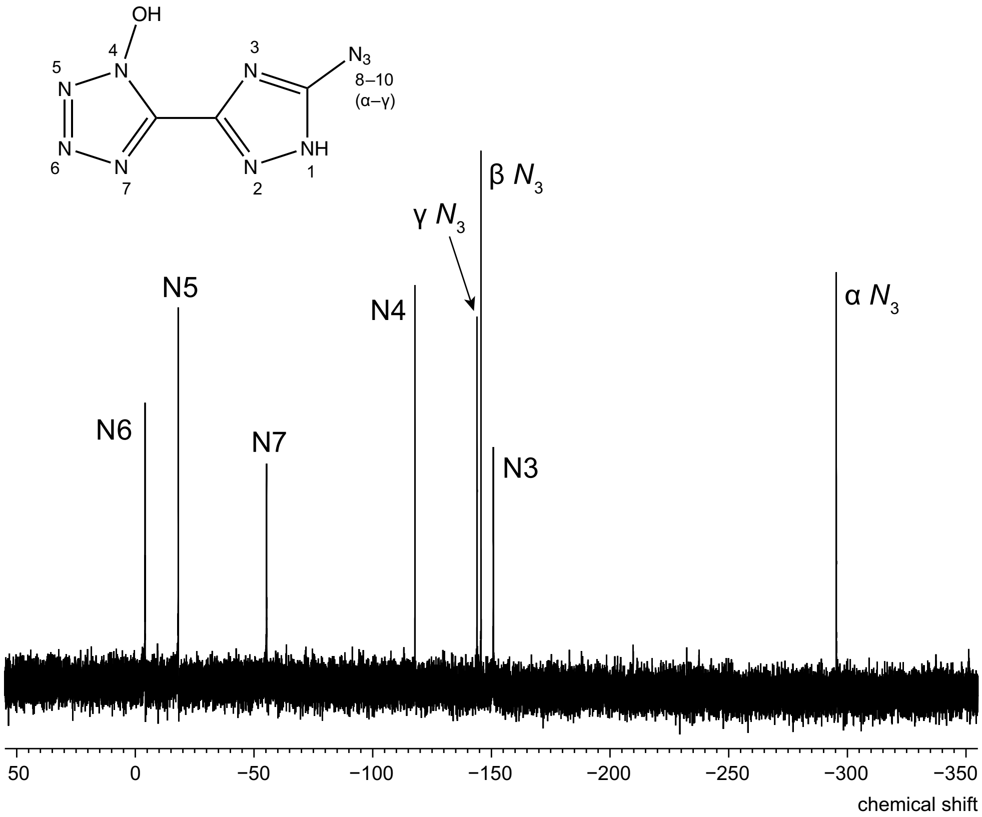


Figure 4.12: ^{15}N NMR spectrum of 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) in DMSO-d_6 at room temperature.

for the nitrogen-rich salts, all with the monovalent anion. The parent compound **20** itself decomposes at 144 °C, after melting at 83 °C. Compared with 5-azido-3-nitro-1H-1,2,4-triazole (**3**) and its salts, the salts of **20** exhibit clearly higher thermal stabilities, as was expected owing to the deprotonation of the tetrazol-1-ol while the C-azido-1,2,4-triazole is left protonated. This is comparable to 5-nitrotetrazol-2-ol and its salts,[149] 5,5′-bis(tetrazol-1-ol) and its salts,[155] 5,5′-bis(tetrazol-2-ol) and its salts,[156] or also 3,4,5-trinitropyrazol-1-ol and most of its salts.[157] The salts with the divalent anion (**25**, **26**, **31**, **32**) are much less thermally stable. The bis(guanidinium) salt **32** already decomposes at 117 °C, which is the lowest value for all the investigated compounds. The not further presented double salts with hydrazine, aminoguanidine and even hydroxylamine all show onset temperatures above 150 °C.

4.2.5 Sensitivities

For initial safety testing the impact and friction sensitivities as well as the electrostatic sensitivities were determined and assigned according to the UN recommendations on the transport of dangerous goods. The neutral compound **20** has to be classified as sensitive, with sensitivities of 4 J to impact and 120 N to friction, after being dried at 60 °C overnight. The metal salts **21** and **23**–**25** are very sensitive to impact with sensitivities of or under 1 J, except for **26** (5 J), and could already be detonated by a hit with a small hammer. The friction sensitivities are similarly high with 5 to 10 N, except for **26** (60 N). As could be expected the silver salt **21** is the most sensitive, but still manageable and no comparison to silver salts like that of 5-azidotetrazol-2-ol.[151] The copper(I) salt (**22**) is completely insensitive to both impact (40 J) and friction (360 N). In contrast to this the nitrogen-rich salts are mostly less sensitive or insensitive (**27**, **29**, **31**, **32**) with impact sensitivities above 35 J and friction sensitivities above 360 N. The only exceptions are the hydrazinium salt **28**, which is interestingly very sensitive to impact (3 J) and sensitive to friction (144 N), and the aminoguanidinium salt **30**, being sensitive to impact (25 J) but insensitive to friction (360 N). Interestingly, the aforementioned bis(hydrazinium) salt is much less sensitive to impact (20 J) then **28**. The metal salts, again except for **22** (800 mJ) and **26** (300 mJ), show the highest sensitivities to electrostatic discharge in the range of primary explosives like lead azide (5 mJ) between 5 and 15 mJ, with **21** being again the most sensitive. The nitrogen-rich salts and **20** are between 150 and 500 mJ. This is comparable to those of similar nitrogen-rich salts or secondary explosives like RDX (200 mJ). The metal salts **21** and **23**–**26** were the only ones to always detonate (impact, friction and electrostatic discharge), while **22** and the nitrogen-rich salts merely only vanished without sound.

4.2.6 Energetic Properties

The metal salts containing the cations silver (**21**), copper(I) (**22**), potassium (**23**, **25**), cesium (**24**) and copper(II) (**26**) were tested for their capability of being true primary explosives and not just highly sensitive compounds. A small amount (approx. 5 mg) of **21**–**26** was heated on a spatula by a lighter, without direct flame contact. All compounds except for the copper(I) salt **22**, which only deflagrated quite unspectacularly, detonated upon reaching their corresponding ignition temperatures. Compound **22** is therefore no primary explosive. Next, a small sample (again approx. 5 mg) of **21** and **23**–**26** was fixed to a surface with a bit of transparent tape and poked with a preheated needle. Disappointingly, only the silver salt **21** detonated while the other salts only deflagrated, although **23** and **24** both showed a very fast deflagration. The potassium salt **23** was nevertheless tested for its capability to initiate the commonly used secondary explosive RDX, similar to **6**. About 400 mg of RDX were loaded in a copper tube (6.50 mm × 57.70 mm), layered with **23** (about 50 mg) and slightly pressed. For the ignition, a commercial type A electrical igniter was used on top,[109] with a direct contact to the primary explosive. Figure 4.13 shows the positive result of this preliminary test setup.

Table 4.5: Energetic properties of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) and its salts **21**–**32**.

Compound	IS / J	FS / N	ESD / mJ	T_d / °C	DDT	fast heating
20	4	120	260	144	—	—
21	1	5	5	184	yes	detonation
22	40	360	800	281	no	—
23	1	6	15	202	yes	deflagration
24	1	10	10	189	yes	deflagration
25	—	—	—	171	—	—
26	5	60	300	157	yes	deflagration
27	35	360	150	180	—	—
28	3	144	150	177	—	—
29	40	360	300	182	—	—
30	25	360	200	171	—	—
31	35	360	150	156	—	—
32	40	360	500	117	—	—

Figure 4.13: Copper tube initiation test of potassium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (**23**) (400 mg RDX, 50 mg **23**). Left: empty copper tube; right: type A igniter (top) and collected remnants after detonation (bottom).

4.3 Conclusions

Several salts of the the novel compound 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) with silver (**21**), copper(I) (**22**), potassium (**23**, **25**), cesium (**24**), copper(II) (**26**), ammonium (**27**, **31**), hydrazinium (**28**), guanidinium (**29**, **32**) and aminoguanidinium (**30**) were prepared and comprehensively characterized, including single crystal X-ray diffraction (**20**, **23** $\cdot$ H_2O, **24**, **25** $\cdot$ 3 H_2O, **27**). The structural investigations prove the higher acidity of the tetrazole bonded hydroxyl group compared to the triazole ring, with the former being always deprotonated first. The thermal stabilities were investigated by differential scanning calorimetry, showing that all salts with the monovalent anion are more stable than neutral **20**. Salts with the divalent anion are much less stable than the monovalent salts and show stabilities approximately equal to **20**. The sensitivities were determined towards common outer stimuli. The salts range from extremely sensitive primary explosives (**21**, **23**–**24**) to insensitive nitrogen-rich compounds (**27**, **29**, **31**, **32**). Most of the metal salts are capable of a DDT when heated slowly. The silver salt **21** further undergoes a fast DDT when heated rapidly with a hot needle. The initiation capability of **23** was positively tested with RDX, using a preliminary test utilizing a copper tube and a commercial igniter. Although the protracted synthesis would need further optimizations (nine steps in total for the salts), especially the metal salts with silver (**21**), potassium (**23**) and cesium (**24**) are interesting materials with good thermal stabilities and non-toxic cations (**23** and **24**) for further investigations.

4.4 Experimental Part

5-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (20)

Sodium azide (1.95 g, 30.0 mmol) in water (27 mL) was added to **17** (3.75 g, 20.0 mmol) in ethanol (33 mL) at 0 °C. The mixture was stirred for 15 minutes at that temperature, then for two hours at room temperature. The suspension was acidified with hydrochloric acid (2 M, 20 mL), stirred for 30 minutes, extracted with diethyl ether (5 × 300 mL) and the combined organic phases were dried over magnesium sulfate. Hydrogen chloride gas was passed into the stirred solution at 0 °C for 75 minutes, whereby the temperature rose up to 19 °C (it should not rise higher!). The flask was stoppered and the resulting solution was stirred for two days at room temperature under a hydrogen chloride overpressure. After evaporation of the solvent to almost complete dryness water was added and completely evaporated at ambient conditions to yield a colorless solid (3.71 g, 17.5 mmol, 80 %). ^{1}H NMR (DMSO-d_6): $\delta = 9.51$ (br). ^{13}C NMR (DMSO-d_6): $\delta = 155.2$ (C2), 144.6 (C1), 139.7 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -136$ (N9). ^{15}N NMR (DMSO-d_6): $\delta = -4.1$ (N6), -18.1 (N5), -55.3 (N7), -117.8 (N4), -144.0 (N10), -145.6 (N9), -150.8 (N3), -295.3 (N8). IR (ATR): $\tilde{\nu} = 3233$ (s), 2477 (w), 2375 (w), 2232 (w), 2154 (vs), 1604 (m), 1535 (vs), 1479 (s), 1336 (s) 1296 (m), 1275 (m), 1223 (m), 1190 (m), 1152 (w), 1129 (m), 1071 (w), 1046 (w), 1014 (w), 982 (m), 855 (w), 781 (m), 753 (w), 712 (w), 696 (w), 658 (w) cm^{-1}. Raman (200 mW): $\tilde{\nu} = 2154(8)$, 1605(100), 1537(20), 1485(10), 1422(8), 1397(4), 1336(12), 1276(17), 1191(2), 1130(5), 1062(2), 1045(6), 1015(5), 980(7), 805(3), 757(3) cm^{-1}. MS (FAB+): $m/z = 195.2$ ($[M+H]^{+}$). MS (FAB−): $m/z = 193.3$ ($[M-H]^{-}$). EA ($C_3H_2N_{10}O \cdot H_2O$): calculated

C 16.99, H 1.90, N 66.03 %; found C 17.53, H 1.87, N 65.16 %. DSC (5 °C min^{-1}): T_m = 83 °C, T_d = 144 °C. Sensitivities (anhydrous, grain size < 100 µm): IS 4 J, FS 120 N, ESD > 260 mJ.

Silver 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (21)

Silver nitrate (340 mg, 2.00 mmol) in water (10 mL) was added drop wise to **20** (424 mg, 2.00 mmol) in water (40 mL) at 65 °C and the resulting suspension was stirred in the dark for 15 minutes. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a colorless powder (459 mg, 1.71 mmol, 86 %). IR (ATR): $\tilde{\nu}$ = 2356 (w), 2133 (s), 1715 (w), 1572 (m), 1493 (m), 1446 (w), 1362 (m), 1237 (s), 1188 (vs), 1082 (w), 1028 (w), 993 (w), 873 (m), 781 (s), 746 (s), 714 (m), 688 (w), 674 (w) cm^{-1}. EA ($C_3HAgN_{10}O$): calculated C 11.97, H 0.33, N 46.54 %; found C 11.85, H 0.00, N 43.90 %. DSC (5 °C min^{-1}): T_d = 184 °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 5 mJ.

Copper(I) 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (22)

A solution of **20** (424 mg, 2.00 mmol) in water (21 mL) and aqueous sodium hydroxide solution (2 M, 1 mL) was added to copper(II) chloride dihydrate (341 mg, 2.00 mmol) in water (14 mL) at 80 °C. The resulting blue suspension was heated to 90 °C and sodium ascorbate (198 mg, 1.00 mmol) in water (1 mL) was added drop wise. The suspension was refluxed for 15 minutes, cooled to room temperature and filtered. The residue was washed with water and ethanol then dried at 60 °C to yield a brownish-green powder (428 mg, 1.67 mmol, 84 %). IR (ATR): $\tilde{\nu}$ = 3443 (s), 3332 (m), 3221 (w), 3062 (w), 2944 (w), 2893 (w), 2710 (m), 2153 (s), 1663 (vs), 1624 (w), 1530 (s), 1494 (w), 1473 (m), 1421 (w), 1372 (w), 1320 (vs), 1256 (vs), 1207 (m), 1143 (m), 1127 (w), 1099 (m), 1062 (w), 1015 (w), 984 (w), 848 (w), 772 (m), 744 (m), 723 (m), 695 (w), 671 (w) cm^{-1}. DSC (5 °C min^{-1}): T_d = 281 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 800 mJ.

General method for salts 23–32

Potassium carbonate (**23**: 1.00 mmol; **25**: 2.00 mmol), cesium carbonate (**24**: 1.00 mmol), copper(II) chloride trihydrate (**26**: 2.00 mmol), aqueous ammonia solution (**27**: 2.00 mmol; **31**: 4.00 mmol), hydrazine monohydrate (**28**: 2.00 mmol), guanidinium carbonate (**29**: 1.00 mmol; **32**: 2.00 mmol), and aminoguanidinium hydrogen carbonate (**30**: 2.00 mmol), respectively, were added to a solution of **20** (424 mg, 2.00 mmol) in ethanol (20 mL), or aqueous sodium hydroxide solution (2.0 mmol, 20 mL) in the case of **26**, and refluxed for 30 minutes. If a solid precipitated then it was filtered off and washed with little ethanol and diethyl ether, then dried in air. If no precipitation occurred then the solvent was evaporated under reduced pressure, the residue washed with very little ethanol and diethyl ether then dried in air. In the case of **24** water was added drop wise to the refluxing ethanolic solution until all solids were dissolved, afterwards proceeded as above.

Potassium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (23)

Colorless powder (368 mg, 1.59 mmol, 80 %). ^{13}C NMR (DMSO-d_6): $\delta = 157.2$ (C2), 144.4 (C1), 134.3 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -134$ (N9). IR (ATR): $\tilde{\nu} = 2237$ (w), 2206 (w), 2146 (vs), 1622 (m), 1497 (m), 1474 (w), 1456 (vs), 1431 (w), 1417 (s), 1349 (vs), 1297 (m), 1233 (vs), 1193 (vs), 1156 (s), 1087 (m), 1019 (m), 991 (m), 857 (s), 795 (m), 757 (m), 744 (m), 729 (m), 700 (w), 687 (w) cm^{-1}. MS (FAB+): $m/z = 39.0$ ([K]$^+$). MS (FAB−): $m/z = 193.3$ ([$C_3HN_{10}O$]$^-$). EA ($C_3HKN_{10}O$): calculated C 15.52, H 0.43, N 60.32 %; found C 15.92, H 0.50, N 59.52 %. DSC (5 °C min^{-1}): $T_d = 202$ °C. Sensitivities (grain size $<$ 100 µm): IS 1 J, FS 6 N, ESD 15 mJ.

Cesium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazol-1-olate (24)

Colorless powder (538 mg, 1.65 mmol, 83 %). ^{13}C NMR (DMSO-d_6): $\delta = 157.2$ (C2), 144.3 (C1), 134.5 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -135$ (N9). IR (ATR): $\tilde{\nu} = 2938$ (w), 2802 (w), 2712 (w), 2451 (w), 2363 (w), 2240 (w), 2155 (vs), 1615 (m), 1501 (vs), 1457 (s), 1418 (s), 1352 (m), 1280 (w), 1226 (vs), 1192 (vs), 1138 (m), 1088 (m), 1011 (m), 984 (m), 855 (s), 792 (w), 756 (w), 746 (m), 728 (m), 698 (w), 679 (w) cm^{-1}. MS (FAB+): $m/z = 133.0$ ([Cs]$^+$). MS (FAB−): $m/z = 193.4$ ([$C_3HN_{10}O$]$^-$). EA ($C_3HCsN_{10}O$): calculated C 11.05, H 0.31, N 42.96 %; found C 11.46, H 0.48, N 42.53 %. DSC (5 °C min^{-1}): $T_d = 189$ °C. Sensitivities (grain size $<$ 100 µm): IS 1 J, FS 10 N, ESD 10 mJ.

Dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate (25)

The compound could not be obtained pure and is contaminated with **23**, even when an excess of potassium carbonate is used. DSC (5 °C min^{-1}): $T_d = 171$ °C (**25**), 210 °C (**23**).

Copper(II) 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate dihydrate (26)

Dark green powder (407 mg, 1.59 mmol, 80 %). IR (ATR): $\tilde{\nu} = 3541$ (w), 3427 (w), 2296 (w), 2149 (vs), 1644 (w), 1547 (w), 1492 (m), 1469 (vs), 1417 (w), 1371 (s), 1269 (s), 1232 (w), 1216 (s), 1166 (w), 1084 (m), 1030 (w), 1012 (m), 824 (w), 772 (m), 752 (w), 728 (m) cm^{-1}. EA ($C_3H_4CuN_{10}O_3$): calculated C 12.37, H 1.38, N 48.02 %; found C 12.74, H 1.46, N 47.43 %. DSC (5 °C min^{-1}): $T_d = 157$ °C. Sensitivities (grain size $<$ 100 µm): IS 5 J, FS 60 N, ESD 300 mJ.

Ammonium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate monohydrate (27)

Colorless powder (311 mg, 1.47 mmol, 74 %). ^{1}H NMR (DMSO-d_6): $\delta = 6.67$ (NH_4^+). ^{13}C NMR (DMSO-d_6): $\delta = 156.5$ (C2), 146.0 (C1), 135.9 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -133$ (N9), -356 (NH_4^+). IR (ATR): $\tilde{\nu} = 3364$ (w), 3009 (w), 2790 (w), 2146 (vs), 1906 (m), 1676 (m), 1560 (m), 1470 (s), 1427 (s), 1348 (m), 1333 (m), 1234 (vs), 1200 (s), 1081 (w), 1043 (m), 1017 (w), 994 (m), 892 (w), 804 (w), 750 (s), 725 (m), 691 (w) cm^{-1}. MS (FAB+): $m/z = 18.1$ ($[NH_4]^+$). MS (FAB−): $m/z = 193.3$ ($[C_3HN_{10}O]^-$). EA ($C_3H_5N_{11}O \cdot H_2O$): calculated C 15.79, H 2.65, N 67.53 %; found C 16.47, H 3.01, N 70.31 %. DSC (5 °C min^{-1}): $T_{\mathrm{dh}} = 125$ °C, $T_{\mathrm{d}} = 180$ °C. Sensitivities (grain size < 100 µm): IS 35 J, FS 360 N, ESD 150 mJ.

Hydrazinium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (28)

Colorless powder (380 mg, 1.68 mmol, 84 %). ^{1}H NMR (DMSO-d_6): $\delta = 6.47$ ($N_2H_5^+$). ^{13}C NMR (DMSO-d_6): $\delta = 156.5$ (C2), 146.1 (C1), 135.8 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -136$ (N9). IR (ATR): $\tilde{\nu} = 3337$ (m), 2994 (m), 2897 (w), 2775 (w), 2602 (w), 2242 (w), 2159 (vs), 1589 (w), 1558 (vs), 1487 (s), 1474 (w), 1426 (vs), 1358 (m), 1324 (m), 1238 (vs), 1205 (w), 1992 (s), 1092 (s), 1032 (s), 986 (s), 932 (s). 797 (m), 754 (s), 718 (s), 695 (w) cm^{-1}. MS (FAB+): $m/z = 33.1$ ($[N_2H_5]^+$). MS (FAB−): $m/z = 193.3$ ($[C_3HN_{10}O]^-$). EA ($C_3H_6N_{12}O$): calculated C 15.93, H 2.67, N 74.32 %; found C 16.52, H 2.61, N 72.82 %. DSC (5 °C min^{-1}): $T_{\mathrm{d}} = 177$ °C. Sensitivities (grain size < 100 µm): IS 3 J, FS 144 N, ESD 150 mJ.

Guanidinium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (29)

Colorless powder (368 mg, 1.45 mmol, 73 %). ^{1}H NMR (DMSO-d_6): $\delta = 6.96$ (NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 157.9$ (G^+), 157.1 (C2), 144.3 (C1), 134.4 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -134$ (N9). IR (ATR): $\tilde{\nu} = 3444$ (w), 3350 (m), 3181 (m), 2220 (w), 2170 (w), 2152 (w), 1652 (vs), 1586 (w), 1500 (vs), 1470 (s), 1433 (m), 1358 (m), 1262 (m), 1214 (s), 1184 (m), 1120 (m), 1004 (w), 987 (m), 728 (s), 660 (m) cm^{-1}. MS (FAB+): $m/z = 60.1$ ($[CH_6N_3]^+$). (FAB−): $m/z = 193.3$ ($[C_3HN_{10}O]^-$). EA ($C_4H_7N_{13}O$): calculated C 18.98, H 2.79, N 71.92 %; found C 19.06, H 2.97, N 69.33 %. DSC (5 °C min^{-1}): $T_{\mathrm{d}} = 182$ °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 300 mJ.

Aminoguanidinium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-olate (30)

Colorless powder (459 mg, 1.71 mmol, 86 %). ^{1}H NMR (DMSO-d_6): $\delta = 8.63$ (s, 1H, NH), 7.26 (s, 2H, C$-NH_2$), 6.83 (s, 2H, C$-NH_2$), 4.70 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): $\delta =$

158.8 (AG^+), 157.2 (C2), 144.3 (C1), 134.5 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -134$ (N9). IR: $\tilde{\nu} = 3375$ (m), 3172 (s), 2163 (vs), 1675 (vs), 1504 (s), 1468 (s), 1434 (m), 1357 (s), 1256 (s), 1227 (w), 1212 (s), 1181 (m), 1122 (s), 1033 (m), 1008 (w), 984 (s), 740 (vs) cm^{-1}. MS (FAB+): $m/z = 75.1$ ($[CH_7N_4]^+$). MS (FAB−): $m/z = 193.3$ ($[C_3HN_{10}O]^-$). EA ($C_4H_8N_{14}O$): calculated C 17.91, H 3.01, N 73.11 %; found C 18.53, H 2.93, N 71.53 %. DSC (5 °C min^{-1}): $T_d = 171$ °C. Sensitivities (grain size < 100 µm): IS 25 J, FS 360 N, ESD 200 mJ.

Diammonium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate (31)

Colorless powder (186 mg, 0.82 mmol, 41 %). ^{1}H NMR (DMSO-d_6): $\delta = 6.41$ (NH_4^+). ^{13}C NMR (DMSO-d_6): $\delta = 156.2$ (C2), 146.6 (C1), 136.4 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -132$ (N9), -359 (NH_4^+). IR (ATR): $\tilde{\nu} = 2761$ (s), 2146 (vs), 1676 (m), 1470 (s), 1427 (vs), 1235 (vs), 1201 (s), 1080 (w), 1044 (m), 994 (m), 750 (m), 726 (m) cm^{-1}. MS (FAB+): $m/z = 18.1$ ($[NH_4]^+$). MS (FAB−): $m/z = 193.3$ ($[C_3HN_{10}O]^-$). EA ($C_3H_8N_{12}O$): calculated C 15.79, H 3.53, N 73.66 %; found C 16.41, H 3.33, N 71.49 %. DSC (5 °C min^{-1}): $T_d = 156$ °C. Sensitivities (grain size < 100 µm): IS 35 J, FS 360 N, ESD 150 mJ.

Bis(guanidinium) 5-(5-azido-1,2,4-triazolate-3-yl)tetrazol-1-olate (32)

Colorless powder (560 mg, 1.79 mmol, 90 %). ^{1}H NMR (DMSO-d_6): $\delta = 7.43$ (NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 158.3$ (G^+), 155.3 (C2), 149.2 (C1), 138.4 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -137$ (N9). IR (ATR): $\tilde{\nu} = 3427$ (w), 3338 (w), 3058 (m), 2228 (w), 2140 (vs), 1654 (vs), 1578 (m), 1508 (w), 1463 (s), 1430 (s), 1345 (w), 1326 (w), 1235 (s), 1202 (m), 1139 (w), 1075 (w), 1034 (m), 1008 (w), 993 (m), 758 (m), 726 (m), 684 (w) cm^{-1}. MS (FAB+): $m/z = 60.1$ ($[CH_6N_3]^+$). MS (FAB−): $m/z = 193.3$ ($[C_3HN_{10}O]^-$). EA ($C_5H_{12}N_{16}O$): calculated C 19.23, H 3.87, N 71.77 %; found C 20.15, H 4.00, N 67.38 %. DSC (5 °C min^{-1}): $T_d = 117$ °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 500 mJ.

5-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazole

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Propellants Explos. Pyrotech. **2014**, *39*, 793–801

5.1 Introduction

The previous chapter demonstrated the benefit of C-C attaching 1-hydroxytetrazole as second energetic group on the azido-1,2,4-triazole backbone for the thermal stability of the salts. Unfortunately, the synthesis is quite protracted with eight steps, and one additional ninth step for salt formation. A rather obvious solution is to employ 1*H*-tetrazole, leading to 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**).[139] Both compounds **20** and **33** can share 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) as an intermediate, which results in a more efficient five step synthesis for **33**.

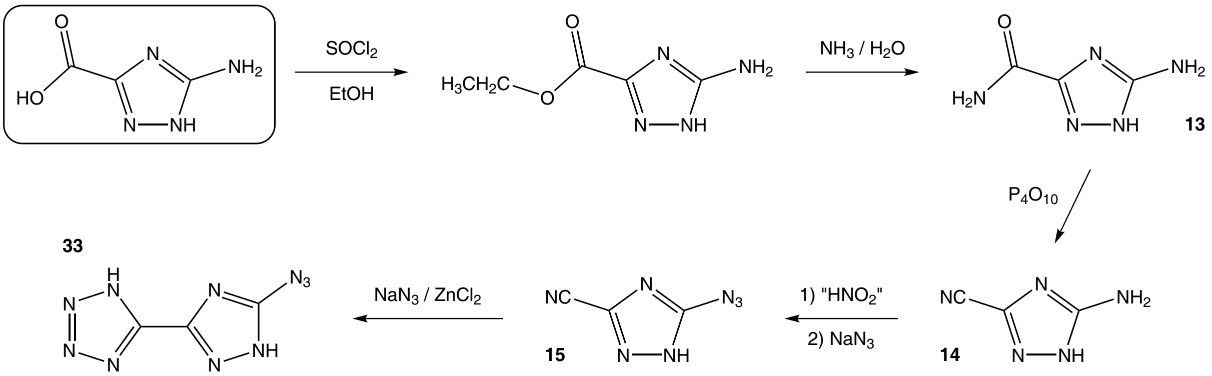
The objective of this study has therefore been the preparation of selected energetic salts of **33** and their comparison with the corresponding salts of **20**.

5.2 Results and Discussion

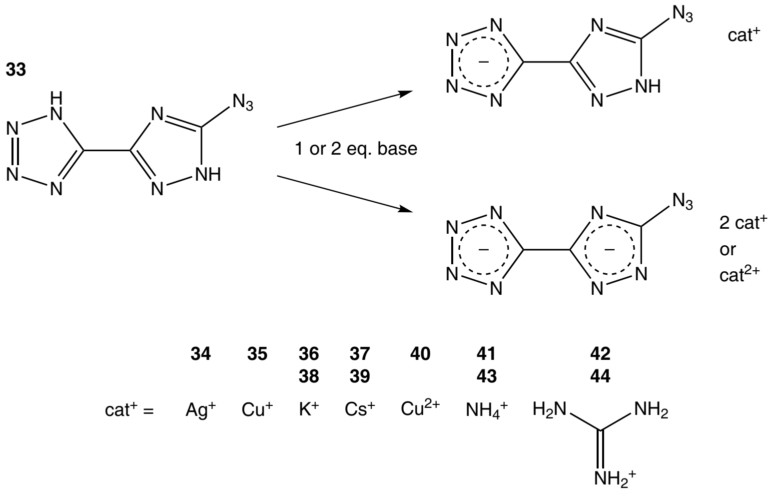
5.2.1 Syntheses

The starting material 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) was synthesized according to a (modified) literature procedure which has been published recently.[139] In the literature procedure, 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) was prepared from 5-amino-1*H*-1,2,4-triazole-3-carbonitrile (**14**) by first converting the nitrile to the tetrazole ring with sodium azide and zinc chloride, yielding 5-(5-amino-1*H*-1,2,4-triazol-3-yl)tetrazole, followed by diazotation with sodium nitrite in 25 % sulfuric acid and subsequent reaction with sodium azide. Another option is to first exchange the amine with the azide, yielding the previously investigated 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**), followed by ring closure, as illustrated in scheme 5.1.

The alkali metal salts with potassium (**36**, **38**) and cesium (**37**, **39**), as well as the nitrogen-rich salts with ammonium (**41**, **43**) and guanidinium (**42**, **44**) were prepared according to scheme 5.2 in ethanolic solution using **33** and the corresponding carbonates or free bases and subsequent precipitation of the salt or evaporation of the solvent under reduced pressure. The silver salt **34** was prepared by the reaction of the neutral compound



Scheme 5.1: Synthetic route towards 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) from commercially available 3-amino-1*H*-1,2,4-triazole-5-carboxylic acid.



Scheme 5.2: Synthesis of the salts **34**–**44** with single and two times deprotonated 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**).

with silver nitrate in water. The copper(I) salt **35** was prepared according to the preparation of DBX-1 by the reaction of the in situ prepared sodium salt of **33** with copper(II) chloride in water and the subsequent reduction of copper(II) to copper(I) using sodium ascorbate.[28] The copper(II) salt **40** was prepared by the reaction of copper(II) chloride with the in situ prepared sodium salt of **33** in water.

5.2.2 Crystal Structure Analysis

The crystal structure of **33** itself has already been determined in the original publication.[139] From the ionic compounds presented in this contribution only the cesium salt **37** could be recrystallized to yield measurable single crystals.

Interestingly, although the compound is a monohydrate, as shown by IR spectroscopy, elemental analysis and DSC, it crystallized with three ion pairs and two water molecules

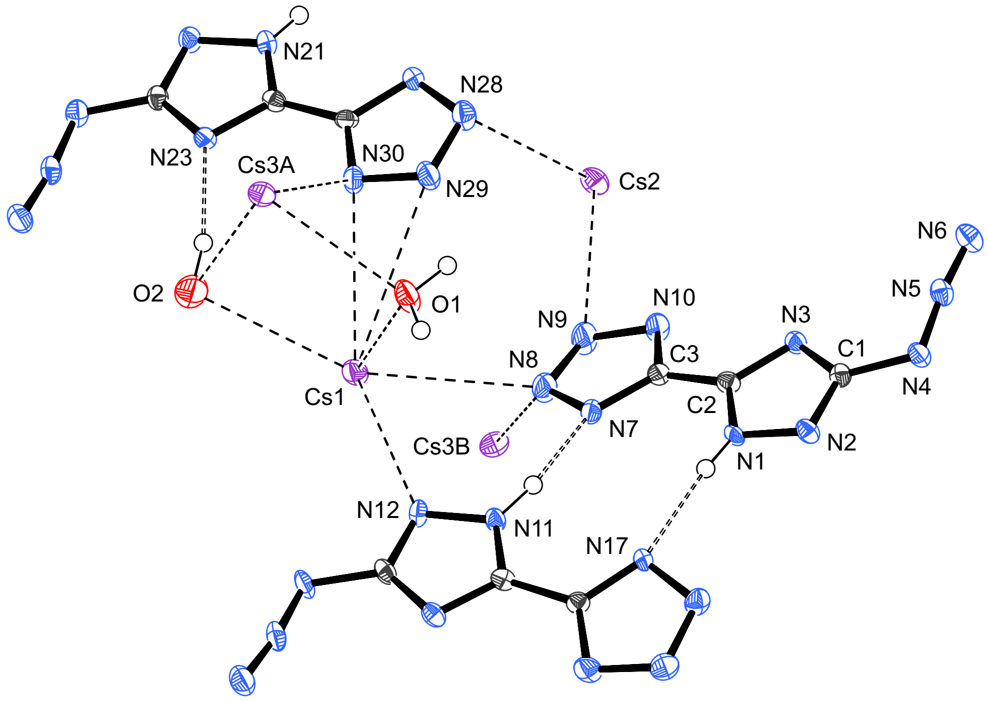


Figure 5.1: Molecular structure of cesium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate ($\mathbf{37} \cdot \frac{2}{3}\,H_2O$). Thermal ellipsoids at 50 % probability.

in the triclinic space group $P\bar{1}$. The molecular moiety is depicted in figure 5.1. One of the cesium cations is disordered with a 63:37 ratio for Cs3A and Cs3B. Resulting from this and the general heavy atom nature of cesium, only three of the four water molecule hydrogen atoms could be located together with the three hydrogen atoms from the three anions. All were either fixed (water molecules) or calculated (HFIX 43, anions) due to slightly distorted positions when refined freely. Similar to the crystal structure of **24**, the nitrogen-bound acidic proton of the triazole ring is relocated to the nitrogen atom beside the C-C bridge from its original position beside the azide (see **33**,[139] **20** and **27**). The structure of the anion is similar to **33** itself. The first two anions are forming dimers in the asymmetric unit, connected by two hydrogen bonds N1–H1···N17 and N11–H11···N7. The third anion similarly forms dimers with itself (N21–H21···$N27^{iii}$) in addition to the third hydrogen bond of the asymmetric unit (O2–H2A···N23). These dimers are further connected to the first water molecule (O1–H1A···$N22^{i}$ and O1–H1B···$N28^{ii}$). A discussion of the bond lengths and angles is omitted due to the idealized positions. The bonding situation is further depicted in figure 5.2.

5.2.3 NMR Spectroscopy

Compounds **36**–**39** and **41**–**44** were analyzed by ^{1}H, ^{13}C and ^{14}N NMR spectroscopy in DMSO-d_6. The numbering of the atoms is according to **33** itself (due to the change of

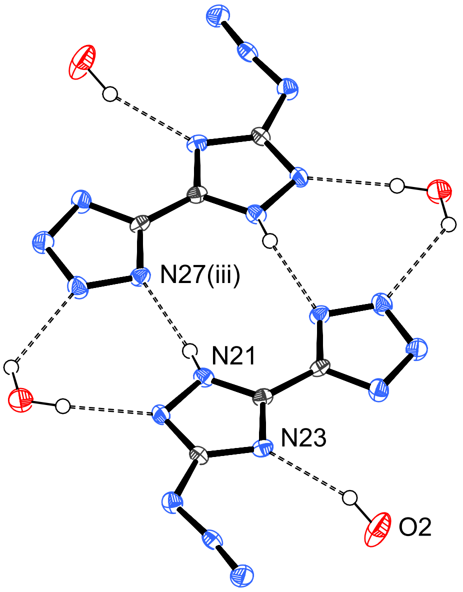


Figure 5.2: Hydrogen bonding of the third AzTT⁻ anion in the crystal structure of cesium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate ($\mathbf{37} \cdot \frac{2}{3}\,H_2O$). Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y, -z+1$.

numbering in the crystal structure of **37**), with N1 being the nitrogen beside the C2-bonded azide. The metal salts **36**–**39** show no visible signal in their corresponding ^{1}H NMR spectrum due to a fast proton exchange in DMSO. The nitrogen-rich salts **41**–**44** show also only one signal between 5.90 and 7.75 ppm, also due to proton exchange. The effect of deprotonation only marginally affects the shifts of the three carbon atoms in the ^{13}C NMR spectra, similar to **20**. While **33** itself displays signals at 155.4 (C2), 148.4 (C3) and 146.1 ppm (C1), the signals of the 1:1 salts **36**, **37**, **41** and **42** are at 156.8 to 157.0 ppm (C2), at 151.7 to 151.9 ppm (C1) and at 149.6 to 149.9 ppm (C3). Compared to the corresponding salts of **20**, C2 shows a similar shift while C3 of the tetrazole ring and also C1 of the triazole ring are both shifted towards lower field. The 2:1 salts **38** and **43** show signals very similar to the 1:1 salts **36** and **41**, probably due to a fast proton exchange. Only **44** is really distinguishable from its 1:1 analogue **42**, with signals at 155.9 (C2), 154.6 (C1) and 153.9 ppm (C3), similar to the guanidinium 1:1 and 2:1 salts of **20**. Compounds **42** and **44** further show the signal of the cation around 158 ppm. The azide beta nitrogen atom is visible as a broad signal in the ^{14}N NMR spectra with a signal maximum between −131 and −135 ppm. Compounds **41** and **43** further show the sharp signal of the ammonium cation around −360 ppm.

5.2.4 Thermal Stabilities

The thermal behavior of the synthesized compounds was investigated by differential scanning calorimetry. In general, the thermal stabilities of the salts of **33** are comparable, or rather almost identical, to those of **20**. The decomposition temperatures of the investigated salts range from 159 °C (**36**) up to 297 °C (**35**) for the metal salts with the monovalent anion and from 144 °C (**40**) to 159 °C (**38**) for those with the divalent anion. Interestingly, the monovalent potassium salt **36** (159 °C) displays an almost identical decomposition onset than the divalent salt **38** (156 °C), while the two compounds are clearly distinguishable by IR spectroscopy, elemental analysis and their color (**36** is almost colorless while **38** is yellow). Compared to the corresponding potassium salts of **20** (**23** and **25**) this is especially interesting because all four salts are prepared in the same way. While **25** decomposes at 171 °C, **23** is stable up to 202 °C. Regarding the cesium salts of both **33** and **20**, the decomposition onsets are more similar (**37**: 183 °C; **24**: 189 °C; **39**: 151 °C; Cs_2AzTTO: 151 °C). The nitrogen-rich salts show the same trend, i.e. the monovalent salts **41** and **42** are more stable (around 163 °C) than the divalent salts **43** and **44** ($<$ 153 °C). The bis(guanidinium) salt **44** again exhibits the lowest decomposition temperature of all the investigated compounds (127 °C), similar to **32** (117 °C).

5.2.5 Sensitivities

The metal salts **34** and **36**–**40** are very sensitive to impact with sensitivities of less or equal than 1 J, except for **40** (2 J), and could already be detonated by a hit with a small hammer. The friction sensitivities are similarly high with 5 to 16 N. As expected, the silver salt **34** is the most sensitive, but still manageable without problems on a small scale. The copper(I) salt **35** is completely insensitive against both impact (40 J) and friction (360 N). In contrast to this the nitrogen-rich salts **41**–**44** are insensitive, with impact sensitivities above 40 J and friction sensitivities above 360 N, except for **41** which exhibits a friction sensitivity of 324 N and therefore being sensitive. The metal salts, again except for **35** (1000 mJ), show the highest sensitivities to electrostatic discharge in the range of primary explosives like lead azide (5 mJ) between 5 and 20 mJ, with **34** being again the most sensitive. The nitrogen-rich salts are between 800 and 1000 mJ and are therefore much less sensitive than RDX (200 mJ), for example. The metal salts **34** and **36**–**40** were the only ones to always detonate (impact, friction and electrostatic discharge), while **35** and the nitrogen-rich salts merely only vanished without sound.

Table 5.1: Energetic properties of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) and its salts **34**–**44**.

Compound	IS / J	FS / N	ESD / mJ	T_d / °C	DDT	fast heating
33	1	20	50	152	—	—
34	1	5	14	180	yes	detonation
35	40	360	1000	297	no	—
36	1	5	5	159	yes	detonation
37	1	16	20	183	yes	deflagration
38	1	14	10	156	yes	detonation
39	1	16	5	151	yes	detonation
40	2	5	15	144	yes	detonation
41	40	324	1000	165	—	—
42	40	360	1000	162	—	—
43	40	360	1000	153	—	—
44	40	360	800	127	—	—

5.2.6 Energetic Properties

The metal salts containing the cations silver (**34**), copper(I) (**35**), potassium (**36**, **38**), cesium (**37**, **39**) and copper(II) (**40**) were tested for their capability of being true primary explosives, and not just highly sensitive compounds. Thus, a small amount (approx. 5 mg) of **34**–**40** was heated on a spatula by a lighter, without direct flame contact. All compounds except for the copper(I) salt **35**, which only deflagrated in a quite unspectacular manner, detonated upon reaching their corresponding ignition temperatures. Compound **35** is therefore no primary explosive at all and similar to **22**. Next, a small sample (again approx. 5 mg) of **34** and **36**–**40** was fixed to a surface with a bit of transparent tape and poked with a preheated needle. Except for the monovalent cesium salt **37**, which only deflagrated, all tested compounds detonated. From the salts of **20**, only the silver salt **21** showed a positive hot-needle test, while the potassium (**23**) and cesium (**24**) salts showed only a (very fast) deflagration. Salts **34** and **36**–**40** can thus be classified as primary explosives, although the DDT of **37** is too slow when heated rapidly.

5.3 Conclusions

Several salts of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) with silver (**34**), copper(I) (**35**), potassium (**36**, **38**), cesium (**37**, **39**), copper(II) (**40**), ammonium (**41**, **43**) and guanidinium (**42**, **44**) were prepared and well characterized. The structure of **37** was determined as **37** $\cdot \frac{2}{3}$ H_2O by low-temperature single crystal X-ray diffraction. The thermal stabilities were analyzed by differential scanning calorimetry. While all salts with the monovalent anion are more stable than neutral **33**, salts with the divalent anion are less stable than the monovalent salts and display stabilities roughly equal to **33**. The sensitivities were determined towards common outer stimuli. The salts range from extremely sensitive primary explosives (**34** and **36**–**40**) to insensitive nitrogen-rich compounds (**41**–**44**). Except for **35** all of the metal salts are capable of a DDT when heated slowly, as well as when heated rapidly with a hot needle (**34**, **36** and **38**–**40**). Although the most interesting salt concerning low toxicity and costs would be the monovalent potassium salt **36**, it is one of the metal salts with the lowest thermal stabilities. Still, the salts with silver (**34**) and cesium (**37**) are interesting materials with good thermal stabilities for further investigations, especially due to the more facile preparation and similar properties (thermal stability, energetic performance, etc.) compared to **20** and its salts.

5.4 Experimental Part

5-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazole (33)

A suspension of **15** (4.05 g, 30.0 mmol), sodium azide (2.15 g, 33.1 mmol) and zinc chloride (5.10 g, 37.4 mmol) in water (150 mL) was refluxed for 18 hours. After cooling to room temperature it was acidified with hydrochloric acid (2 M, 25.5 mL) and the resulting clear yellow solution was extracted with ethyl acetate (4 × 250 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was washed with diethyl ether to yield an off-white powder (4.62 g, 25.9 mmol, 86 %). ^{1}H NMR (DMSO-d_6): $\delta = 15.26$ (br). ^{13}C NMR (DMSO-d_6): $\delta = 155.4$ (C2), 148.4 (C3), 146.1 (C1). ^{14}N NMR (DMSO-d_6): $\delta = -138$ (N9). IR (ATR): $\tilde{\nu} = 3141$ (w), 3052 (w), 2930 (w), 2862 (w), 2382 (w), 2236 (w), 2147 (vs), 1624 (s), 1544 (vs), 1484 (s), 1392 (s), 1324 (w), 1264 (s), 1194 (vs), 1140 (m), 1082 (m), 1054 (w), 1043 (m), 1012 (w), 981 (s), 800 (m), 763 (w), 726 (s), 695 (s) cm^{-1}. EA ($C_3H_2N_{10}$): calculated C 20.23, H 1.13, N 78.64 %; found C 21.21, H 1.34, N 76.08 %. DSC (5 °C min^{-1}): $T_d = 152$ °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 20 N, ESD 50 mJ.

Silver 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate (34)

Silver nitrate (170 mg, 1.00 mmol) in water (20 mL) was added drop wise to **33** (178 mg, 1.00 mmol) in water (20 mL) at 80 °C and the resulting suspension was stirred in the dark for 30 minutes at 70 °C. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a colorless powder (262 mg, 919 µmol, 92 %). IR (ATR): $\tilde{\nu} =$ 2976 (w), 2908 (w), 2807 (w), 2421 (w), 2324 (w), 2207 (w), 2190 (m), 2152 (s), 1587 (s), 1540 (vs), 1494 (w), 1470 (m), 1407 (m), 1374 (s), 1305 (w), 1280 (vs), 1218 (s), 1198 (m), 1167 (s), 1107 (w), 1066 (w), 1049 (s), 1020 (s), 988 (m), 829 (m), 790 (s), 773 (w), 725 (vs), 690 (m) cm^{-1}. EA (C_3HAgN_{10}): calculated C 12.64, H 0.35, N 49.15 %; found C 12.70, H 0.66, N 47.03 %. DSC ($5\,^\circ\text{C}\,\text{min}^{-1}$): $T_\text{d} = 180\,^\circ\text{C}$. Sensitivities (grain size $< 100\,\mu\text{m}$): IS 1 J, FS 5 N, ESD 14 mJ.

Copper(I) 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate (35)

A solution of **33** (356 mg, 2.00 mmol) in water (6 mL) and aqueous sodium hydroxide solution (2 M, 1 mL) was added to copper(II) chloride dihydrate (341 mg, 2.00 mmol) in water (14 mL) at 80 °C. The resulting blue suspension was heated to 90 °C and sodium ascorbate (198 mg, 1.00 mmol) in water (1 mL) was added drop wise. The suspension was refluxed for 30 minutes, cooled to room temperature and filtered. The residue was washed with water and ethanol then dried at 60 °C to yield a green-grey powder (367 mg, 1.53 mmol, 77 %). IR (ATR): $\tilde{\nu} = 3156$ (w), 2142 (vs), 1634 (w), 1547 (m), 1460 (vs), 1396 (s), 1329 (s), 1203 (s), 1144 (m), 1093 (w), 1072 (w), 999 (m), 805 (w), 723 (s) cm^{-1}. DSC ($5\,^\circ\text{C}\,\text{min}^{-1}$): $T_\text{d} = 297\,^\circ\text{C}$. Sensitivities (grain size $< 100\,\mu\text{m}$): IS 40 J, FS 360 N, ESD 1000 mJ.

General method for salts 36–44

Potassium carbonate (**36**: 1.00 mmol; **38**: 2.00 mmol), cesium carbonate (**37**: 1.00 mmol; **39**: 2.00 mmol), copper(II) chloride trihydrate (**40**: 2.00 mmol), aqueous ammonia solution (**41**: 2.00 mmol; **43**: 4.00 mmol) and guanidinium carbonate (**42**: 1.00 mmol; **44**: 2.00 mmol), respectively, were added to a solution of **33** (356 mg, 2.00 mmol) in ethanol (20 mL), or aqueous sodium hydroxide solution (2.0 mmol, 20 mL) in the case of **40**, and refluxed for 30 minutes. If a solid precipitated then it was filtered off and washed with little ethanol and diethyl ether, then dried in air. If no precipitation occurred then the solvent was evaporated under reduced pressure, the residue washed with very little ethanol and diethyl ether then dried in air. In the case of **36**, **37** and **39** water was added drop wise to the refluxing ethanolic solution until all solids were dissolved, afterwards proceeded as above.

Potassium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate (36)

Pale yellow powder (382 mg, 1.76 mmol, 88 %). ^{13}C NMR (DMSO-d_6): $\delta = 156.9$ (C2), 151.9 (C1), 149.8 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -131$ (N9). IR (ATR): $\tilde{\nu} = 3606$ (w), 3419 (w), 3122 (w), 3014 (m), 2910 (w), 2837 (m), 2684 (m), 2562 (w), 2248 (w), 2142 (w), 2127 (w), 1766 (w), 1618 (w), 1512 (w), 1500 (m), 1445 (vs), 1379 (s), 1319 (s), 1281 (s), 1231 (s), 1207 (m), 1199 (w), 1144 (w), 1126 (w), 1087 (m), 1060 (w), 1038 (w), 1020 (w), 1011 (w), 996 (s), 890 (s), 760 (w), 768 (w), 736 (m), 730 (w), 690 (w) cm^{-1}. MS (FAB+): $m/z = 39.0$ ($[\text{K}]^+$); (FAB−): $m/z = 177.3$ ($[C_3HN_{10}]^-$). EA (C_3HKN_{10}): calculated C 16.67, H 0.47, N

64.78 %; found C 16.69, H 1.00, N 61.69 %. DSC (5 °C min^{-1}): T_d = 159 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 5 N, ESD 5 mJ.

Cesium 5-(3-azido-1*H*-1,2,4-triazol-5-yl)tetrazolate monohydrate (37)

Colorless powder (493 mg, 1.59 mmol, 80 %). ^{13}C NMR (DMSO-d_6): δ = 157.0 (C2), 151.9 (C1), 149.6 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -135$ (N5). IR (ATR): $\tilde{\nu}$ = 3431 (w), 3110 (w), 3008 (w), 2832 (w), 2700 (w), 2361 (w), 2156 (s), 1610 (m), 1510 (w), 1500 (w), 1445 (vs), 1373 (s), 1317 (s), 1270 (m), 1233 (s), 1184 (w), 1144 (w), 1124 (w), 1076 (m), 1018 (m), 993 (s), 878 (w), 766 (w), 734 (w), 728 (w) cm^{-1}. MS (FAB+): m/z = 133.0 ($[\text{Cs}]^+$). MS (FAB−): m/z = 177.3 ($[\text{C}_3\text{HN}_{10}]^-$). EA ($\text{C}_3\text{HCsN}_{10} \cdot \text{H}_2\text{O}$): calculated C 10.98, H 0.92, N 42.70 %; found C 11.71, H 1.08, N 43.00 %. DSC (5 °C min^{-1}): T_dh = 120 °C, T_d = 183 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 16 N, ESD 20 mJ.

Dipotassium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazolate (38)

Yellow powder (448 mg, 1.76 mmol, 88 %). ^{13}C NMR (DMSO-d_6): δ = 156.9 (C2), 152.1 (C1), 149.9 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -134$ (N9). IR (ATR): $\tilde{\nu}$ = 3124 (w), 3013 (w), 2834 (w), 2699 (w), 2142 (w), 2126 (w), 1618 (w), 1512 (w), 1500 (m), 1445 (vs), 1379 (s), 1319 (s), 1280 (m), 1230 (m), 1207 (w), 1144 (w), 1126 (w), 1087 (w), 1060 (w), 1038 (w), 1020 (w), 1010 (w), 995 (s), 886 (m), 846 (w), 736 (m), 692 (w), 666 (w) cm^{-1}. MS (FAB+): m/z = 39.0 ($[\text{K}]^+$). MS (FAB−): m/z = 177.3 ($[\text{C}_3\text{HN}_{10}]^-$). EA ($\text{C}_3\text{K}_2\text{N}_{10}$): calculated C 14.17, H 0.00, N 55.08 %; found C 15.56, H 0.89, N 53.14 %. DSC (5 °C min^{-1}): T_d = 156 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 14 N, ESD 10 mJ.

Dicesium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazolate (39)

Yellow-orange powder (743 mg, 1.62 mmol, 81 %). IR (ATR): $\tilde{\nu}$ = 2456 (w), 2210 (w), 2127 (vs), 2034 (w), 1654 (w), 1564 (w), 1465 (m), 1452 (w), 1422 (s), 1376 (m), 1310 (m), 1271 (s), 1246 (m), 1176 (m), 1119 (w), 1092 (w), 1069 (w), 1025 (m), 990 (m), 792 (m), 726 (s) cm^{-1}. MS (FAB+): m/z = 133.0 ($[\text{Cs}]^+$). MS (FAB−): m/z = 177.3 ($[\text{C}_3\text{HN}_{10}]^-$). EA ($\text{C}_3\text{Cs}_2\text{N}_{10}$): calculated C 8.15, N 31.07 %; found C 8.54, N 32.04 %. DSC (5 °C min^{-1}): T_d = 151 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 16 N, ESD 5 mJ.

Copper(II) 5-(5-azido-1,2,4-triazolate-3-yl)tetrazolate (40)

Green powder (225 mg, 939 µmol, 47 %). IR (ATR): $\tilde{\nu}$ = 3332 (s), 3166 (m), 2962 (w), 2779 (w), 2137 (m), 1666 (vs), 1607 (w), 1536 (m), 1459 (m), 1423 (m), 1390 (m), 1303 (s), 1207 (w), 1128 (w), 1099 (w), 1057 (w), 1016 (w), 988 (w), 810 (m), 761 (m), 732 (s) cm^{-1}. EA

(C_3CuN_{10}): calculated C 15.04, H 0.00, N 58.45 %; found C 15.72, H 0.92, N 58.33 %. DSC (5 °C min^{-1}): T_d = 144 °C. Sensitivities (grain size < 100 µm): IS 2 J, FS 5 N, ESD 15 mJ.

Ammonium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate (41)

Pale yellow powder (174 mg, 891 µmol, 40 %). ^{1}H NMR (DMSO-d_6): δ = 7.16 (NH_4^+). ^{13}C NMR (DMSO-d_6): δ = 156.8 (C2), 151.7 (C1), 149.6 (C3). ^{14}N NMR (DMSO-d_6): δ = −134 (N9), −354 (NH_4^+). IR (ATR): $\tilde{\nu}$ = 3024 (m), 2856 (m), 2364 (w), 2241 (w), 2138 (vs), 1875 (w), 1668 (w), 1610 (w), 1512 (s), 1447 (vs), 1375 (s), 1319 (s), 1268 (w), 1225 (s), 1192 (w), 1148 (w), 1086 (w), 1062 (w), 1043 (w), 1020 (m), 997 (s), 850 (m), 776 (w), 733 (2), 728 (2), 686 (2), cm^{-1}. MS (FAB+): m/z = 18.1 ($[NH_4]^+$). MS (FAB−): m/z = 177.2 ($[C_3HN_{10}]^-$). EA ($C_3H_5N_{11}$): calculated C 18.46, H 2.58, N 78.95 %; found C 18.56, H 2.95, N 72.71 %. DSC (5 °C min^{-1}): T_d = 165 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 324 N, ESD 1000 mJ.

Guanidinium 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazolate (42)

Colorless powder (451 mg, 1.90 mmol, 86 %). ^{1}H NMR (DMSO-d_6): δ = 7.02 (NH_2). ^{13}C NMR (DMSO-d_6): δ = 157.9 (G^+), 156.9 (C2), 151.8 (C1), 149.6 (C3). ^{14}N NMR (DMSO-d_6): δ = −132 (N9). IR (ATR): $\tilde{\nu}$ = 3348 (w), 3177 (w), 2830 (w), 2141 (s), 1673 (vs), 1496 (m), 1455 (s), 1383 (m), 1323 (m), 1274 (w), 1224 (w), 1197 (w), 1150 (w), 1065 (w), 999 (m), 850 (w), 764 (w), 732 (m) cm^{-1}. MS (FAB+): m/z = 60.1 ($[CH_6N_3]^+$). MS (FAB−): m/z = 177.3 ($[C_3HN_{10}]^-$). EA ($C_4H_7N_{13}$): calculated C 20.26, H 2.97, N 76.77 %; found C 19.86, H 3.24, N 72.13 %. DSC (5 °C min^{-1}): T_d = 162 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 1000 mJ.

Diammonium 5-(5-azido-1,2,4-triazolate-3-yl)tetrazolate (43)

Pale yellow powder (202 mg, 952 µmol, 48 %) ^{1}H NMR (DMSO-d_6): δ = 5.90 (NH_4^+). ^{13}C NMR (DMSO-d_6): δ = 156.7 (C2), 152.2 (C1), 150.1 (C3). ^{14}N NMR (DMSO-d_6): δ = −132 (N9), −361 (NH_4^+). IR (ATR): $\tilde{\nu}$ = 3351 (m), 3178 (w), 3025 (m), 2899 (w), 2822 (w), 2228 (w), 2146 (s), 2119 (m), 2037 (w), 1908 (m), 1703 (m), 1576 (w), 1440 (vs), 1383 (s), 1336 (w), 1283 (m), 1246 (m), 1196 (m), 1135 (w), 1108 (w), 1090 (w), 1072 (w), 1047 (w), 1004 (w), 794 (w), 733 (m), 713 (w) cm^{-1}. MS (FAB+): m/z = 18.1 ($[NH_4]^+$). MS (FAB−): m/z = 177.3 ($[C_3HN_{10}]^-$). EA ($C_3H_8N_{12}$): calculated C 16.98, H 3.80, N 79.22 %; found C 17.54, H 3.49, N 77.41 %. DSC (5 °C min^{-1}): T_d = 153 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 1000 mJ.

Bis(guanidinium) 5-(5-azido-1,2,4-triazolate-3-yl)tetrazolate (44)

Yellow powder (446 mg, 1.51 mmol, 76 %). ^{1}H NMR (DMSO-d_6): $\delta = 7.75$ (NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 158.4$ (G^+), 155.9 (C2), 154.6 (C1), 153.9 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -132$. IR (ATR): $\tilde{\nu} = 3465$ (w), 3435 (w), 3045 (w), 2433 (s), 2135 (vs), 1696 (w), 1644 (vs), 1596 (w), 1576 (w), 1472 (m), 1426 (s), 1378 (m), 1321 (w), 1289 (m), 1222 (m), 1185 (w), 1136 (w), 1103 (w), 1075 (w), 1031 (w), 1001 (w), 802 (w), 771 (w), 728 (m) cm^{-1}. MS (FAB+): $m/z = 60.1$ ($[CH_6N_3]^+$). MS (FAB−): $m/z = 177.3$ ($[C_3HN_{10}]^-$). EA ($C_5H_{12}N_{16}$): calculated C 20.27, H 4.08, N 75.65 %; found C 21.01, H 3.94, N 73.78 %. DSC (5 °C min^{-1}): $T_d = 127$ °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 800 mJ.

1-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazole

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6.1 Introduction

The previous two chapters both employed a C-C linked tetrazole bound to the azido-1,2,4-triazole. As mentioned in the introduction of chapter 4 another, more energetic option is the C-N connection between the two heterocycles. Although the resulting 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**) would lose the significant advantage of the C-C linked **20** and **33**, namely the possibility of deprotonating the tetrazole instead of the triazole, it still seems worthy of investigation. Tetrazoles are electron deficient aromatics, thus it would be interesting to compare the electron withdrawing effect of a non-deprotonatable tetrazole on the thermal stability of salts with that of other electron withdrawing energetic groups like the nitro or cyano groups, which were employed in 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) and 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**). Additionally, due to **49** being a constitutional isomer of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) a comparison of their properties (thermal stability, sensitivity towards outer stimuli, enthalpy of formation, etc.) is of further interest.

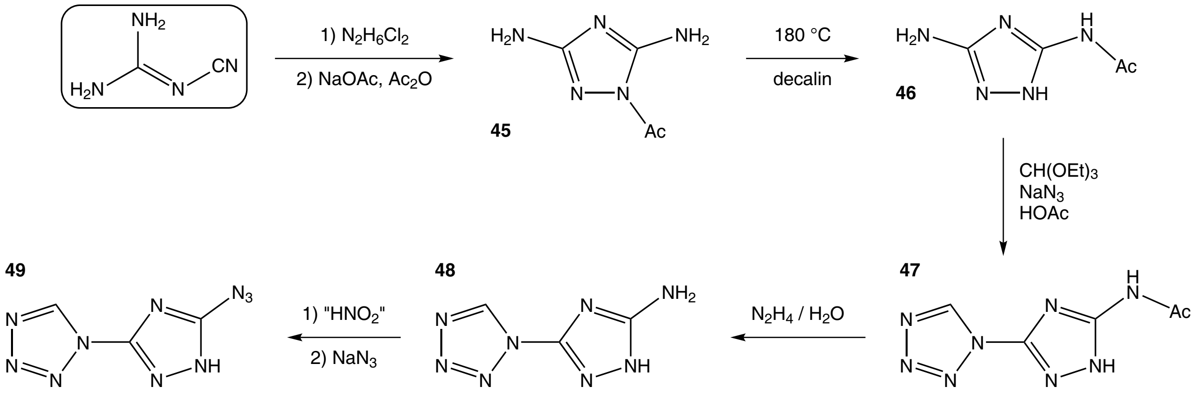
The goal of this study has therefore been the preparation and characterization of **49**, and the comparison to its isomer **33** and **20** (the hydroxy derivative of **33**), especially regarding the thermal stabilities and sensitivities towards external stimuli.

During the investigations another group independently published a successful synthesis of 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole.[159] Interestingly, that report states a decomposition temperature of 223 °C, a figure this study strongly contests.

6.2 Results and Discussion

6.2.1 Synthesis

The first step was the synthesis of 1-acetyl-3,5-diamino-1,2,4-triazole (**45**).[160,161] The literature described method is the direct reaction of the rather expensive 3,5-diamino-1*H*-1,2,4-triazole (DAT) with acetic anhydride, resulting in yields around 80 %. A more cost-effective way on a laboratory scale is the synthesis of DAT utilizing cyanoguanidine and hydrazinium dichloride, which can be reacted with acetic anhydride directly in the



Scheme 6.1: Synthetic route towards 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**) from commercially available cyanoguanidine.

reaction mixture after neutralization with sodium acetate.[162] The resulting yield of **45** was around 64 %. Isolation and purification of the DAT intermediate is not necessary, and is also rather complicated, often resulting in low yields. The next step was the rearrangement of **45** to 5-acetamido-3-amino-1*H*-1,2,4-triazole (**46**) at temperatures above 180 °C,[160,161] thus resulting in the protection of one of the amino groups. The two isomers are easy to distinguish due to the much lower solubility of **46** in practically all common solvents, as well as the shift of the C=O vibration from 1710 to 1682 cm^{-1} in the IR spectra. The remaining free amine was then reacted with triethyl orthoformate and sodium azide in acetic acid, similarly to the method first described by Gaponik and co-workers for various primary amines,[163] to yield 1-(5-acetamido-1*H*-1,2,4-triazol-3-yl)tetrazole (**47**).[164] Although a previous study on this particular compound reported a yield around 80 %, only starting material could be recovered without any trace of the desired product. Even variations in the amount of acetic acid, heating time or heating temperature did not yield any product. While the utilization of trifluoroacetic acid as solvent resulted in a clear solution (acetic acid gives a slurry), it still did not yield any detectable product. Only stirring of the reaction mixture for several days at room temperature prior to heating overnight finally yielded the desired result. Further reaction of **47** with hydrazine hydrate resulted in the deprotection of the amine, yielding 1-(5-amino-1*H*-1,2,4-triazol-3-yl)tetrazole (**48**).[164] The final step was diazotation with sodium nitrite in sulfuric acid, followed by reaction with sodium azide to yield the title compound 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**). Unfortunately, it was not possible to prepare a silver salt due to the attempts always resulting in a brown slurry.

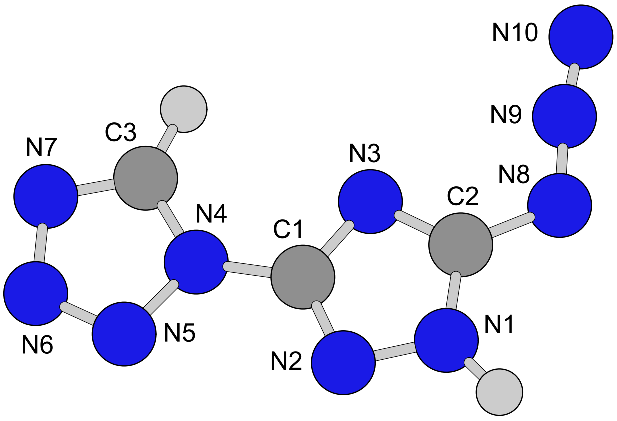


Figure 6.1: Calculated structure of 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**), showing the atom numbering scheme (B3LYP/aug-cc-pVDZ). C1–N4 1.401 Å, N8–N9–N10 171.95°, N3–C1–N4–N5 179.99°, N3–C2–N8–N9 0.00°.

6.2.2 Characterization

The ^{1}H NMR spectrum only shows the signal of the tetrazole CH proton at 10.10 ppm. The NH proton of the triazole could not be observed, probably due to its acidity and thus fast exchange in DMSO-d_6. The ^{13}C NMR spectrum shows, as expected, three signals at 151.6 (C2), 150.4 (C1) and 142.9 ppm (C3). The shift of the tetrazole carbon atom (C3) is similar to the shift found in 1*H*-tetrazole (142.9 ppm),[165] 1-phenyltetrazole (140.5 ppm),[166] 1,2-di(tetrazol-1-yl)ethane (144.3 ppm),[167] and 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**, 143.8 ppm), and quite different from the C-bonded tetrazole of **33** (148.4 ppm). The corresponding shifts of the amine precursor **48** are located at 157.6 (C2), 150.1 (C1) and 142.7 ppm (C3). The broad signal observed in the ^{14}N NMR spectrum at −139 ppm ($\nu_{\frac{1}{2}} = 384$ Hz) can be attributed to the azide beta nitrogen atom (N9), owing to its sufficiently high linear symmetry and the absence of a lone pair. Tetrazole and triazole nitrogen atoms are usually not visible in a ^{14}N NMR spectrum due to their lone pairs and the delocalized electron systems, resulting in strong line broadening. On the other hand, all ten atoms exhibit clearly observable signals in the ^{15}N NMR spectrum (figure 6.2). The tetrazole moiety exhibits signals at 12.0 (d, $^{3}J_{NH} = 3.43$ Hz, N6), −20.2 (N5), −52.4 (d, $^{2}J_{NH} = 12.11$ Hz, N7) and −147.3 ppm (d, $^{2}J_{NH} = 9.29$ Hz, N4), matching the reported shifts for 1-aryltetrazoles very well,[168] and also those found in **79**.[169] The signals at −119.4 (N2), −166.8 (N3) and −185.7 ppm (N1) can be attributed to the triazole moiety and are also in accordance with other *C*-azido-1,2,4-triazoles like **3**, **20** and **33**. The three remaining signals at −143.8 (N9/N10), −146.0 (N10/N9) and −293.8 ppm (N8) belong to the azido group,[170] and also show similar shifts to the aforementioned *C*-azido-1,2,4-triazoles. For the clear assignment of N9 and N10 a ^{15}N labeled azide would be needed, because the gamma atom can display a lower high field shift than the beta atom when the azide is connected to an electron deficient

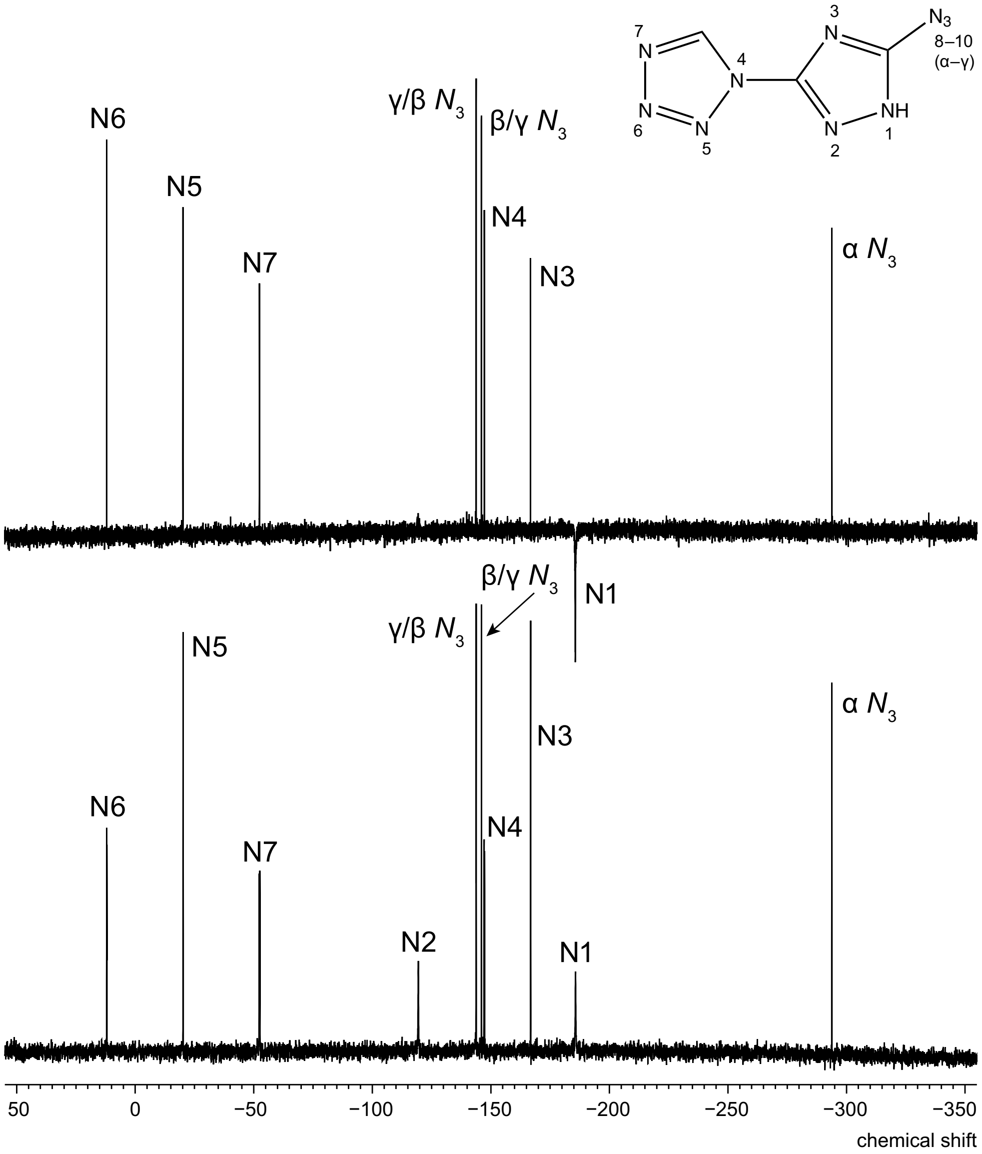


Figure 6.2: ^{15}N and ^{15}N{^{1}H} NMR spectra of 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**) in DMSO-d_6 at room temperature.

system.[171,172] Quantum-chemical calculations (MPW1PW91/aug-cc-pVDZ) indicated that in this particular case N10 has indeed the lower high field shift, similar to 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**) and 5-azido-3-nitro-1*H*-1,2,3-triazole (**3**), but the intensities of the signals at −143.8 and −146.0 ppm in **49** are almost identical, while in the spectra of **20** and **3** the assumed beta nitrogen atom has a noticeably higher intensity than the gamma nitrogen atom.

The only clearly assignable band in the rather complicated IR spectrum is the stretching mode of the terminal azide bond at 2156 cm^{-1}, which is also present in the Raman spectrum at 2166 cm^{-1}.

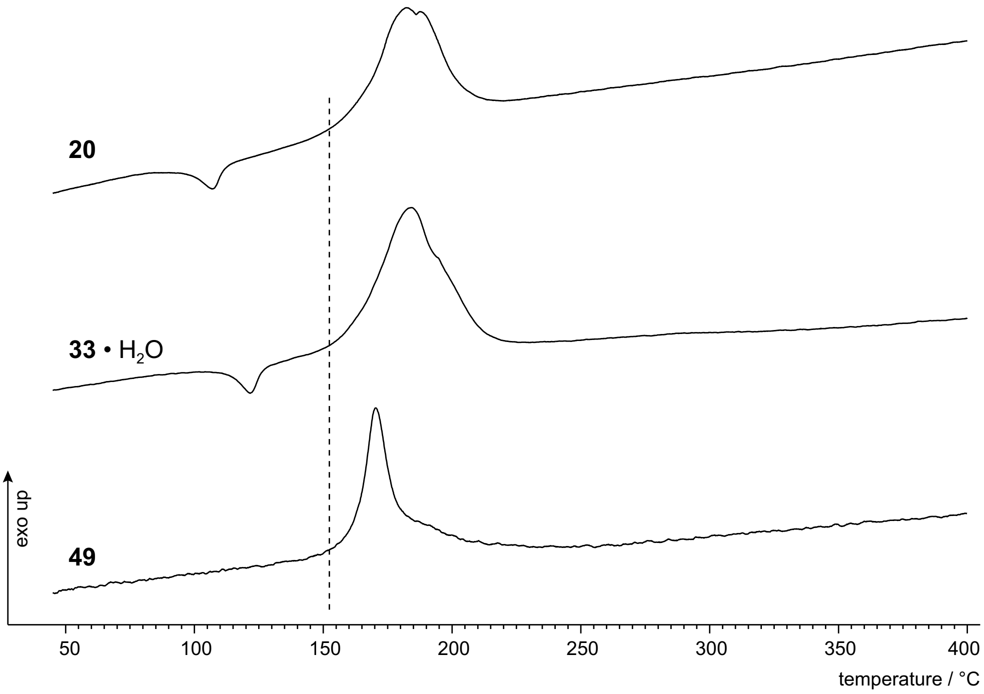


Figure 6.3: DSC plots for 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**), 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole dihydrate (**33** · H_2O) and 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**) at a heating rate of 5 °C min^{-1}. The dashed line indicates the decomposition onset.

The most striking result is the thermal stability (152 °C), which is practically equal to that of **33** and **20**. Interestingly, the third isomer **72** with a 1,2,3-triazole backbone also shows an identical decomposition onset (see later on). The DSC plots of **33**, **20** and **49** are presented in figure 6.3. The two endotherms are loss of crystal water (**33**; measurement was performed with the dihydrate) and melting (**20**). The nitramine analogue 1-(5-nitramino-1*H*-1,2,4-triazol-3-yl)tetrazole reportedly decomposes at 91 °C.[164]

Unfortunately, it was not possible to obtain single crystals for X-ray diffraction, utilizing several solvents and techniques.

6.2.3 Energetic Properties

Regarding the sensitivities, **49** has to be classified as sensitive to impact (4 J) and extremely sensitive to friction (10 N). These values are comparable to **33** (1 J, 20 N) and **20** (4 J, 120 N), although **33** is surprisingly more sensitive to impact, while **20** is much less sensitive to friction.

The enthalpies of formation of **49** and **33** were calculated at the CBS-4M level of theory. According to the calculations, the tautomer of **49** in which the proton is attached to the nitrogen atom in proximity to the tetrazole ring has a lower energy than the tautomer in which the proton is attached to the nitrogen in proximity to the azide (see **33** or **20**), although the difference is practically negligible (0.49 kJ mol^{-1}). Thus, the latter was used for the following calculations and the numbering of the atoms (see figure 6.1). The molecule itself shows a completely planar structure (both CBS-4M and B3LYP/aug-cc-pVDZ), similar to **33**, with a C1–N4 single bond (1.401 Å) connecting the two rings. The aforementioned 1-(5-nitramino-1*H*-1,2,4-triazol-3-yl)tetrazole on the other hand consists of two twisted rings in the crystal structure,[164] but the torsion angle was not given. As expected, the C-N linked isomer **49** exhibits a higher enthalpy of formation (819.0 kJ mol^{-1}) than the C-C linked isomer **33** (779.5 kJ mol^{-1}).

6.3 Conclusions

The goal of the present study has been the preparation and characterization of the novel energetic nitrogen-rich heterocycle 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**). The capability for salt formation was tested with silver nitrate, but unfortunately always resulted in a brown slurry. The capability to form ionic primary explosives was therefore not further investigated. It is nevertheless quite interesting to see that the linkage to the azide is apparently even weaker than that to the C-N bonded tetrazole, resulting in practically identical decomposition onsets for the isomers **33** and **49** (and the hydroxy derivative **20** of **33**) around 150 °C, independent of the type and linkage of the tetrazole ring. The sensitivities towards external stimuli are comparable for the three compounds.

6.4 Experimental Part

1-Acetyl-3,5-diamino-1,2,4-triazole (45)

Cyanoguanidine (85.0 g, 1.00 mol) and hydrazinium dichloride (105 g, 1.00 mol) were stirred in water (200 mL) for four hours at 60 °C. The reaction mixture was neutralized with a solution of sodium acetate (90.4 g, 1.10 mol) in water (300 mL). Acetic anhydride (123 g, 1.20 mol) was added drop wise at room temperature and the suspension was stirred for one hour. The precipitate was filtered off, washed with water and ethanol, and then suspended in ethanol and refluxed for five minutes. The precipitate was filtered off to yield a colorless powder (89.7 g, 636 mmol, 64 %). ^{1}H NMR (DMSO-d_6): δ = 7.38 (s, 2H, NH_2), 5.66 (s, 2H, NH_2), 2.34 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ = 170.5, 162.1, 157.0, 23.5. IR (ATR): $\tilde{\nu}$ = 3415 (w), 3389 (m), 3297 (w), 3130 (m), 1710 (s), 1641 (vs), 1568 (s), 1449 (m), 1392 (s), 1366 (vs), 1337 (s), 1178 (m), 1117 (m), 1066 (m), 1044 (s), 973 (s), 839 (m), 758 (m), 699 (m), 670 (w), 656 (s) cm^{-1}. MS (DEI+): m/z = 141.2 ([M]$^+$), 99.2 ([M$-$C$_2$H$_3$O]$^+$). DSC (5 °C min^{-1}): T_r = 213 °C, T_d = 269 °C. EA ($C_4H_7N_5O$): calculated C 34.04, H 5.00, N 49.62 %; found C 33.89, H 4.81, N 49.59 %.

5-Acetamido-3-amino-1*H*-1,2,4-triazole (46)

A suspension of **45** (60.0 g, 425 mmol) in decalin (750 mL) was heated for seven hours at 180 °C without stirring. The precipitate was filtered off and washed with ethanol and diethyl ether to yield a very fine, pale brown powder (59.6 g, 422 mmol, 99 %). IR (ATR): $\tilde{\nu} = 3422$ (w), 3250 (m), 2953 (w), 2869 (w), 2824 (w), 2166 (w), 1682 (s), 1597 (vs), 1582 (vs), 1450 (s), 1375 (m), 1360 (m), 1295 (s), 1267 (s), 1159 (w), 1080 (s), 1041 (w), 1024 (m), 1006 (m), 833 (w), 817 (w), 759 (w), 712 (s), 687 (m) cm^{-1}. DSC (5 °C min^{-1}): $T_\text{d} = 273$ °C. EA ($C_4H_7N_5O$): calculated C 34.04, H 5.00, N 49.64 %; found C 34.23, H 4.87, N 49.46 %.

1-(5-Acetamido-1*H*-1,2,4-triazol-3-yl)tetrazole (47)

Acetic acid (350 mL) was added in one portion to a stirred mixture of **46** (35.3 g, 250 mmol), sodium azide (19.5 g, 300 mmol) and triethyl orthoformate (55.6 g, 365 mmol). A reflux condenser was attached and the resulting suspension was stirred first for 72 hours at room temperature, and then for 20 hours at 90 °C. Concentrated hydrochloric acid (30 mL) was added after cooling to room temperature (evolution of HN_3!) and stirred for one hour. The solvent was evaporated under reduced pressure, the residue was fully suspended in toluene (about 150 mL) and stirred for about one hour, then again evaporated to dryness. This procedure was repeated once more. The residue was then suspended in water (250 mL) and refluxed until the solid was fully suspended. The precipitate was filtered off, washed with water and dried at 102 °C to yield a pale brown powder (35.1 g, 181 mmol, 72 %). IR (ATR): $\tilde{\nu} = 3315$ (w), 3230 (m), 3107 (m), 1687 (vs), 1589 (vs), 1577 (vs), 1559 (vs), 1530 (s), 1492 (s), 1367 (s), 1324 (w), 1263 (s), 1248 (vs), 1188 (w), 1160 (w), 1117 (w), 1088 (s), 1068 (m), 1040 (w), 1014 (m), 1003 (m), 979 (m), 953 (w), 906 (w), 791 (m), 777 (w), 737 (s), 690 (w), 656 (w) cm^{-1}. MS (DEI+): $m/z = 195.1$ ($[\text{M}]^+$). EA ($C_5H_6N_8O$): calculated C 30.93, H 3.11, N 57.71 %; found C 32.11, H 3.67, N 51.26 %.

1-(5-Amino-1*H*-1,2,4-triazol-3-yl)tetrazole (48)

A mixture of **47** (35.1 g, 181 mmol) and hydrazine hydrate (36.2 g, 724 mmol) was stirred for three hours at 100 °C, then cooled to room temperature. Water (30 mL) was added and the solution was acidified with hydrochloric acid (10 %) to pH 6. The suspension was stirred for 30 minutes, after which the precipitate was filtered off and washed with moderate amounts of water, ethanol and diethyl ether, then finally dried at 102 °C to yield a pale brown powder (5.22 g, 34.3 mmol, 19 %). ^{1}H NMR (DMSO-d_6): $\delta = 11.88$ (vbr, NH), 9.91 (s, 1H, CH), 6.66 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 157.6$ (C2), 150.1 (C1), 142.7 (C3). IR (ATR): $\tilde{\nu} = 3385$ (w), 3257 (w), 3160 (w), 3097 (w), 1650 (vs), 1570 (s), 1518 (vs), 1452 (m), 1423 (w), 1330 (w), 1275 (m), 1192 (w), 1163 (w), 1096 (m), 1078 (m), 1021 (w), 980 (s), 960 (w), 897 (w), 755 (w), 724 (w), 707 (w) cm^{-1}. MS (DEI+): $m/z = 153.2$ ([M]$^+$). EA ($C_3H_4N_8$): calculated C 23.69, H 2.65, N 73.66 %; found C 24.16, H 3.15, N 70.50 %.

1-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazole (49)

Sodium nitrite (414 mg, 6.00 mmol) in water (10 mL) was added drop wise to a suspension of **48** (761 mg, 5.00 mmol) in sulfuric acid (25 %, 30 mL) at 0 °C. The suspension was allowed to warm up to room temperature, followed by stirring for 30 minutes at 40 °C. A small amount of urea was added after cooling to room temperature, followed by the drop wise addition of sodium azide (1.30 g, 20.0 mmol) in water (10 mL). The reaction mixture was stirred overnight, then extracted with ethyl acetate (3 × 75 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was taken up in a minimal amount of ethyl acetate, mixed with *n*-pentane (about 200 mL) and the resulting precipitate was filtered off to yield a colorless solid (629 mg, 3.53 mmol, 71 %). ^{1}H NMR (DMSO-d_6): $\delta = 10.10$ (s, CH). ^{13}C NMR (DMSO-d_6): $\delta =$ 151.6 (C2), 150.4 (C1), 142.9 (C3). ^{14}N NMR (DMSO-d_6): $\delta = -139$ (N9). ^{15}N NMR (DMSO-d_6): $\delta = 12.0$ (d, $^3J_{NH} = 3.43$ Hz, N6), −20.2 (N5), −52.4 (d, $^2J_{NH} = 12.11$ Hz, N7), −119.4 (N2), −143.8 (N9/N10), −146.0 (N10/N9), −147.3 (d, $^2J_{NH} = 9.29$ Hz, N4), −166.8 (N3), −185.7 (N1), −293.8 (N8). IR (ATR): $\tilde{\nu} = 3310$ (m), 3167 (m), 3080 (m), 2932 (w), 2856 (w), 2237 (w), 2156 (vs), 1646 (w), 1572 (m), 1552 (vs), 1534 (vs), 1510 (vs), 1493 (vs), 1440 (m), 1411 (m), 1391 (m), 1353 (m), 1329 (m), 1312 (m), 1286 (m), 1266 (s), 1257 (s), 1191 (s), 1174 (m), 1160 (m), 1107 (m), 1088 (vs), 1043 (m), 1030 (m), 1006 (m), 982 (m), 975 (m), 965 (m), 917 (w), 870 (w), 792 (m), 721 (s), 682 (w), 667 (w) cm^{-1}. Raman (300 mW): 3168 (6), 2166 (15), 1572 (100), 1559 (10), 1535 (5), 1508 (11), 1461 (8), 1398 (22), 1330 (10), 1264 (14), 1255 (5), 1193 (5), 1175 (6), 1090 (7), 1035 (6), 1011 (29) cm^{-1}. MS (DEI+): $m/z = 178.2$ ([M]$^+$). EA ($C_3H_2N_{10}$): calculated C 20.23, H 1.13, N 78.64 %; found C 20.63, H 1.71, N 73.66 %. DSC (5 °C min^{-1}): $T_d = 152$ °C. Sensitivities (grain size < 100 µm): IS 4 J, FS 10 N, ESD 100 mJ.

Silver Salts of Various Azido-1,2,4-triazoles

unpublished results

7.1 Introduction

This final chapter on azido-1,2,4-triazoles deals with the shortcoming of the respective anions in terms of their thermal stabilities, when compared to the corresponding neutral molecules. As already stated in chapter 2, the deprotonation of tetrazoles usually leads to salts with much higher thermal stabilities than the corresponding neutral compounds.[153] During investigations with azido-1,2,4-triazoles it was found that none of the salts of 3-azido-1*H*-1,2,4-triazole (**50**) and 3,5-diazido-1*H*-1,2,4-triazole had a higher thermal stability than the parent compound.[56] 5-Azido-3-nitro-1*H*-1,2,4-triazole (**3**) and 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) with their highly electron withdrawing groups seemed less affected by this, although not by much. Unfortunately, it was not possible to test 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**) in this manner due to the failed attempts of preparing even the silver salt. The recently investigated 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**), for example, is reported with a decomposition temperature of 143 °C, while all nitrogen-rich salts show higher thermal stabilities.[108] The potassium salt (**60**) is reported to explode in the vicinity of 195 °C.[173]

The objective of this chapter has therefore been the preparation of several reported, and some new, simple azido-1,2,4-triazoles with various molecule groups as the second substituent on the ring and the investigation of the applicability of the corresponding, and currently not reported, silver salts as primary explosives.

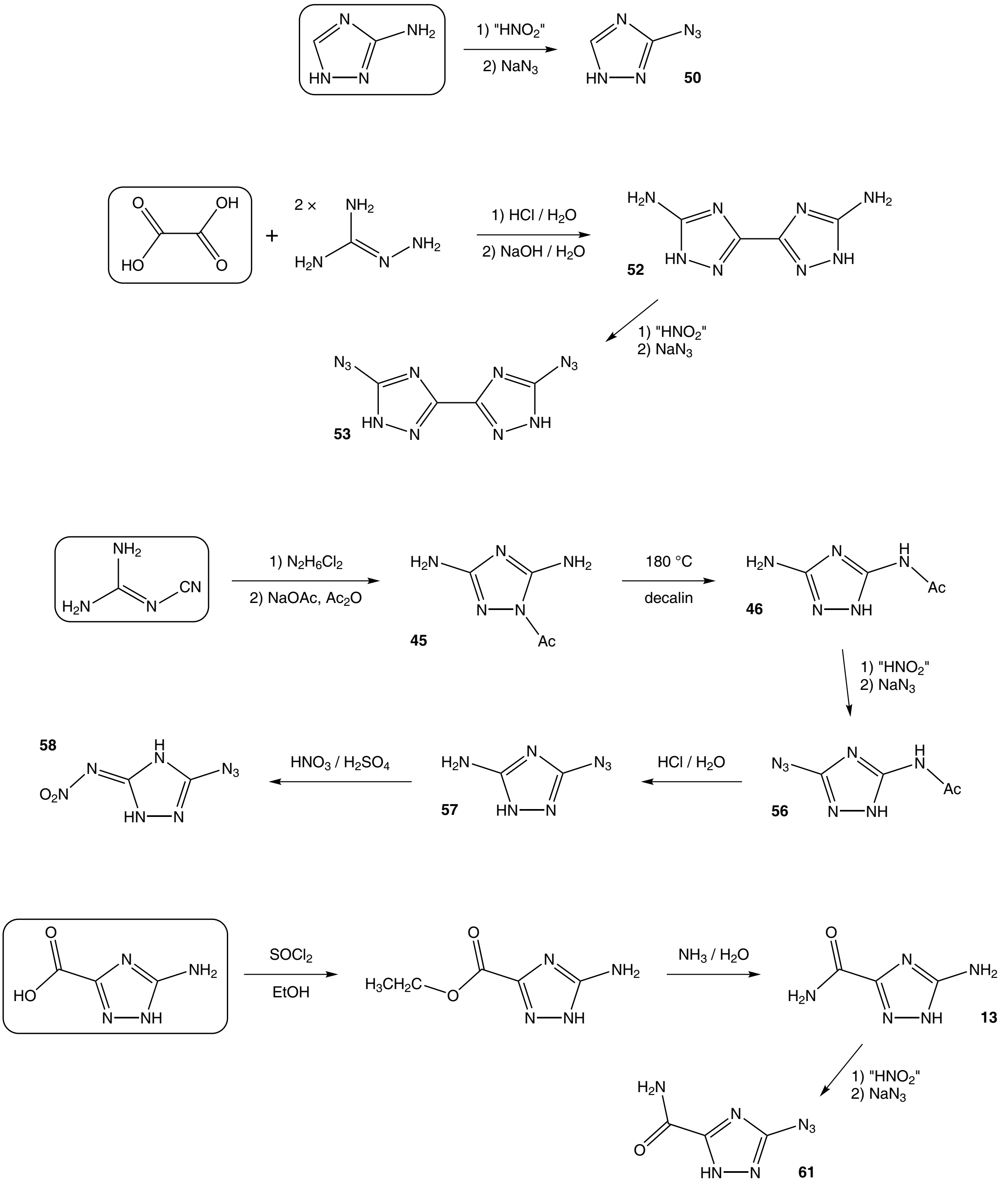
7.2 Results and Discussion

7.2.1 Syntheses

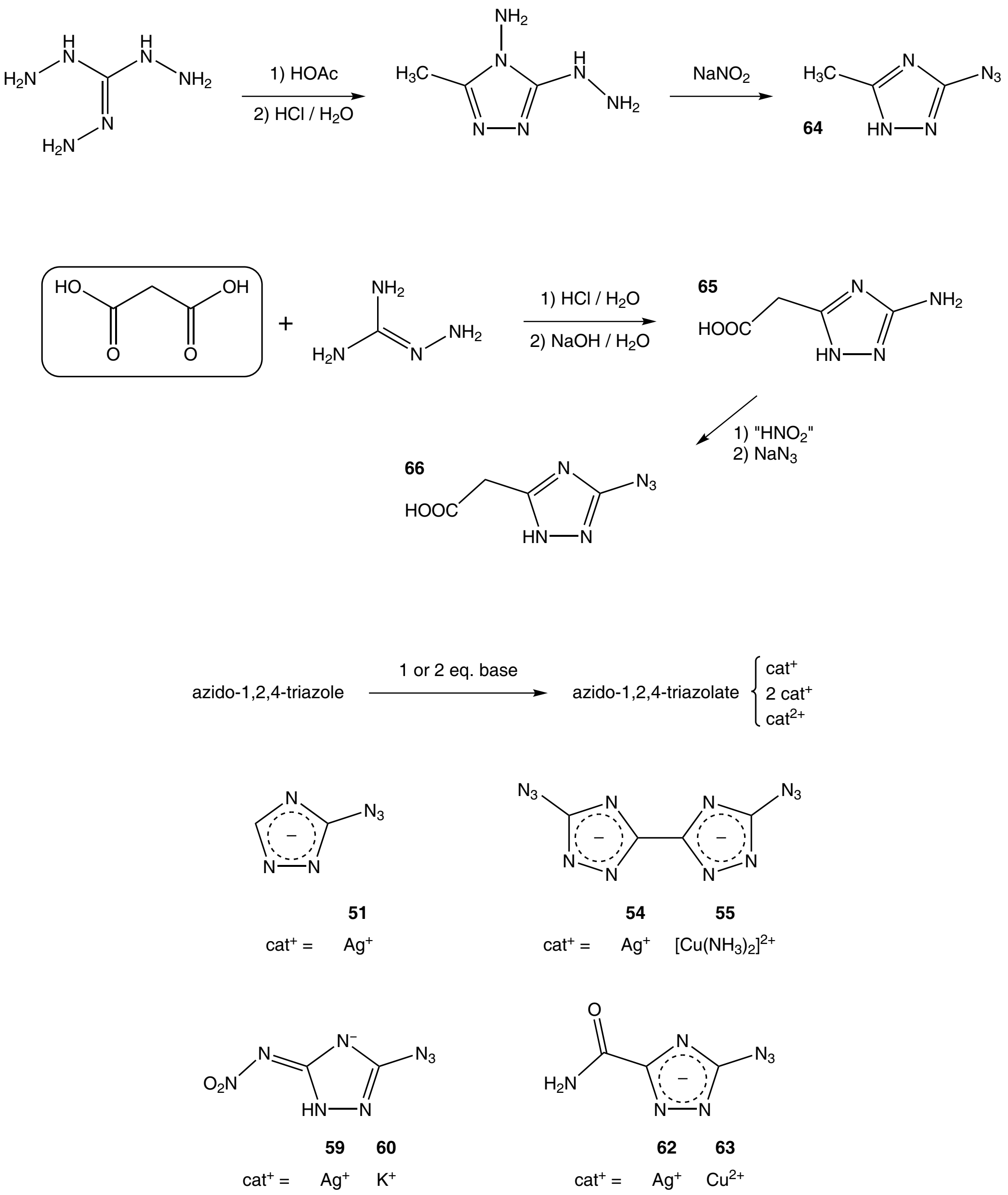
3-Azido-1*H*-1,2,4-triazole (**50**) was prepared from 5-amino-1*H*-1,2,4-triazole by diazotation with sodium nitrite in 25 % sulfuric acid and subsequent reaction with sodium azide.[174]

5,5′-Diazido-3,3′-bis(1*H*-1,2,4-triazole) (**53**) was prepared similarly to **50** from 5,5′-diamino-3,3′-bis(1*H*-1,2,4-triazole) (**52**),[106] which was, in turn, obtained by the reaction of oxalic acid with aminoguanidium carbonate.[175]

For the synthesis of 5-amino-3-azido-1*H*-1,2,4-triazole (**57**) two routes are possible. The shorter one is the synthesis of 3,4,5-triamino-1,2,4-triazole from dimethyl cyanamide



Scheme 7.1: Synthetic routes towards 3-azido-1*H*-1,2,4-triazole (**50**), 5,5′-diazido-3,3′-bis(1*H*-1,2,4-triazole) (**53**), 5-amino-3-azido-1*H*-1,2,4-triazole (**57**), 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**) and 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) from commercially available compounds.



Scheme 7.2: Synthetic routes towards 3-azido-5-methyl-1*H*-1,2,4-triazole (**64**) and 2-(3-azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**) from commercially available compounds, and the metal salts **51**, **54**, **55**, **59**, **60**, **62** and **63**.

and hydrazine,[176,177] and subsequent diazotation with sodium nitrite in acetic acid.[178] Unfortunately, the yield of the intermediate was only between 12 and 25 %, depending on the purity, with a total maximum yield of 6 % for **57**. The second method is the diazotation of 5-acetamido-3-amino-1*H*-1,2,4-triazole (**46**) and subsequent reaction with sodium azide similarly to **50**,[179] followed by deprotection with hydrochloric acid.[179] The total yield of the thus obtained **57** was 16 %. 3-Azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**) was obtained by the subsequent nitration of **57** with nitric acid in sulfuric acid.[108,173]

The novel compound 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) was obtained by the diazotation of 3-amino-1*H*-1,2,4-triazole-5-carboxamide (**13**) and subsequent reaction with sodium azide similarly to **50**.

3-Azido-5-methyl-1*H*-1,2,4-triazole (**64**) was prepared by the reaction of triaminoguanidinium chloride with acetic acid and subsequent diazotation of the intermediate chloride salt with sodium nitrite.[180]

Lastly, the also novel compound 2-(3-azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**) was obtained similarly to **50** from 2-(3-amino-1*H*-1,2,4-triazol-5-yl)acetic acid (**65**), which was, in turn, prepared by the reaction of malonic acid with aminoguanidium carbonate.[181] The synthesis however often resulted in large amounts of an insoluble orange byproduct and would need further optimizations. The compound was intended as precursor molecule for 5-azido-3-trinitromethyl-1*H*-1,2,4-triazole, but nitration attempts similarly to 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole[182] were not yet successful.

The silver salts of **50**,[56] **53**, **58** and **61** were prepared in the usual way by the addition of silver nitrate in water to a warm solution of the corresponding neutral compound in water. Several attempts were performed with **57** and **64**, but unfortunately the obtained brown (silver 5-amino-3-azido-1,2,4-triazolate) or colorless (silver 3-azido-5-methyl-1,2,4-triazolate) solids could not be identified properly. The already reported potassium salt **60** of the nitramine **58** was prepared by the reaction of potassium carbonate with neutral **58** in ethanol and subsequent removal of the solvent under reduced pressure.[173] The diamminecopper(II) salt **55** of **53** was prepared by the addition of copper(II) nitrate to **53** in aqueous ammonia solution. The other attempted metal salts of **53** with iron(II), cobalt(II), nickel, copper(II) and zinc resulted in dark solutions with dark brownish precipitates and were thus discarded. The copper(II) salt **63** of **61** was prepared by the addition of copper(II) sulfate to the in situ prepared sodium salt of **61** in water.

7.2.2 Crystal Structure Analysis

While 3-azido-1*H*-1,2,4-triazole (**50**) usually crystallizes solvent free from aqueous solutions,[183] also evidenced during the course of this thesis, one reaction with **50** as starting material yielded single crystals of the as of yet unknown monohydrate. It crystallized in the orthorhombic spacegroup $Pna2_1$ with four molecules in the unit cell. While the triazole ring itself is identical to that in the anhydrous form the azido moiety is rotated by 180° and pointing now into the opposite direction of the ring attached proton (figure 7.1), similar to most of the compounds in this work. The calculated energy difference between the two isomers of **50** is only $2.46\,\mathrm{kJ\,mol^{-1}}$ in the gas phase (B3LYP/aug-cc-pVDZ), with the orientation seen in $\mathbf{50}\cdot\mathrm{H_2O}$ being the more stable one. The structure features three strong

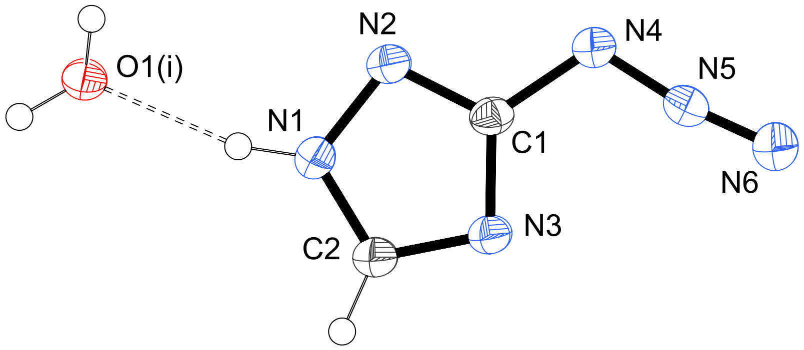


Figure 7.1: Molecular structure of 3-azido-1*H*-1,2,4-triazole monohydrate (**50** · H_2O). Thermal ellipsoids at 50 % probability. Symmetry code: (i) $-x + 1.5, y - 0.5, z - 0.5$.

Table 7.1: Hydrogen bonds present in 3-azido-1*H*-1,2,4-triazole monohydrate (**50** · H_2O).

D–H· · · A	d(D–H) / Å	d(H· · · A) / Å	d(D· · · A) / Å	∠(D–H· · · A) / °
O1–H3· · · N3	0.85(3)	1.96(3)	2.803(2)	177(3)
N1–H1· · · O1^{i}	0.89(2)	1.91(2)	2.778(2)	165(2)
O1–H4· · · O1^{ii}	0.89(3)	1.84(3)	2.726(2)	173(2)

Symmetry codes: (i) $-x + 1.5, y - 0.5, z - 0.5$, (ii) $-x + 2, -y + 1, z - 0.5$.

and well directed hydrogen bonds involving all the nitrogen and oxygen bound protons (table 7.1), resulting in a complicated three dimensional network with no special motifs.

2-(3-Azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**) crystallized as a monohydrate in the monoclinic spacegroup $P2_1/c$ with four molecules in the unit cell. The bond lengths and angles of the heterocyclic core are similar to the other 1,2,4-triazoles in this work and the molecule itself shows a quite planar assembly (N3–C1–N4–N5: −8.7(2)°; N3–C2–C3–C4: −174.4(1)°; O2–C4–C3–C2: 174.8(1)°). The molecule features an undirected intramolecular hydrogen bond between the ring amine and the carboxylic acid oxygen as N1–H1· · · O1 (D· · · A: 2.709(1) Å; D–H· · · A: 116(1)°), resulting in a six membered ring. A second, intermolecular, hydrogen bond between N1 and O1 (D· · · A: 2.867(1) Å; D–H· · · A: 154(1)°) results in the formation of dimers (figure 7.2), which are further strengthened by involvement of the water molecule acting both as acceptor and donor for two additional strong and directed hydrogen bonds in the form of O2–H4· · · O3^{ii} (D· · · A: 2.587(1) Å; D–H· · · A: 174(1)°) and O3–H6· · · N2^{iv} (D· · · A: 2.872(1) Å; D–H· · · A: 175(1)°). The dimers are further connected to chains by an N· · · N short contact between the beta and gamma atoms of the azide (N5· · · N6^{vii}: 3.080(2) Å; symmetry code: (vii) $-x, -y, -z + 1$). These chains are connected by the water molecules through a highly directed O3–H5· · · N3^{iii} hydrogen bond (D· · · A: 2.881(1) Å; D–H· · · A: 177(1)°) which results in a shifted wave-like structure (figure 7.3). The parameters of the hydrogen bonds are compiled in table 7.2.

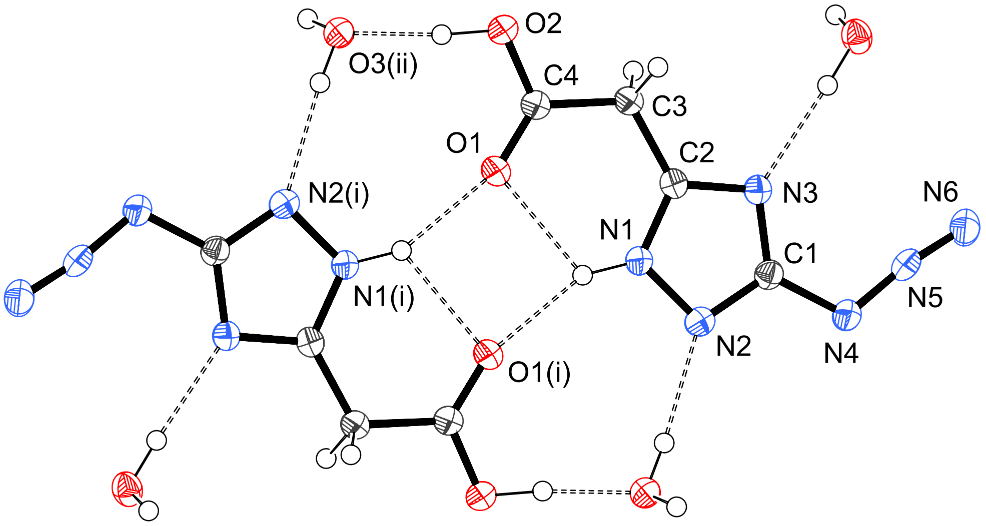


Figure 7.2: Formation of dimers in the crystal structure of 2-(3-azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**). Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x+2, -y, -z$, (ii) $x, -y+0.5, z-0.5$.

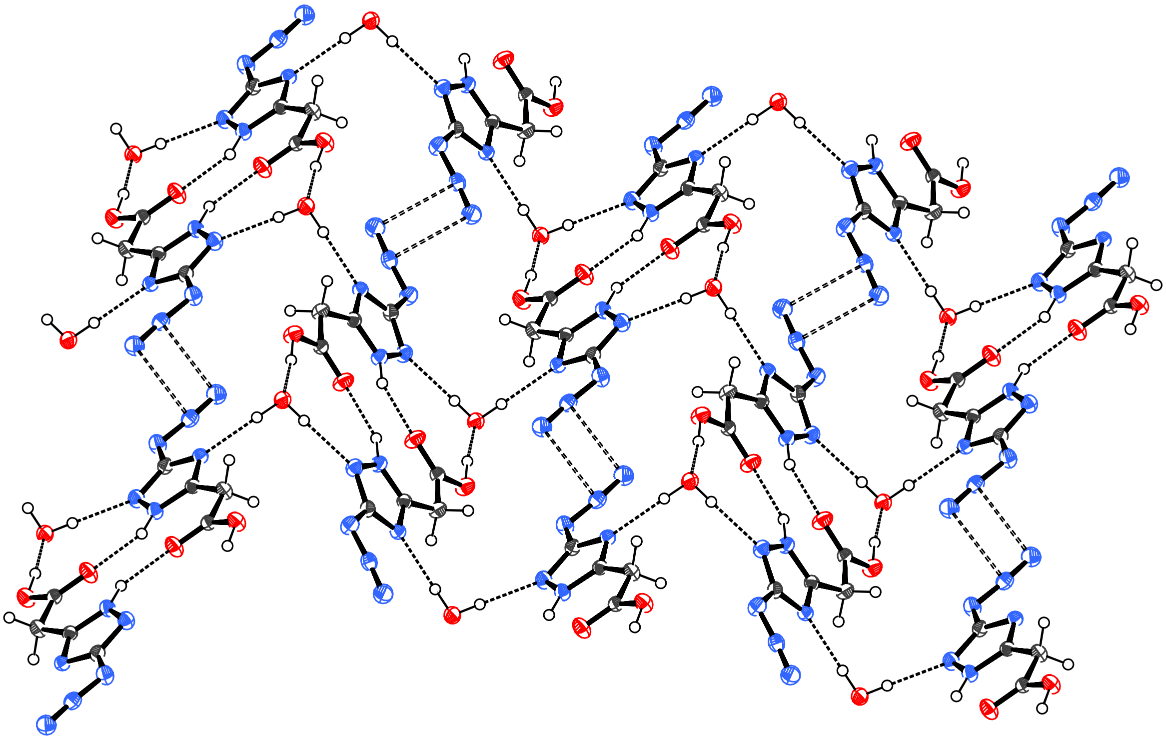


Figure 7.3: Wave-like structural motif of 2-(3-azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**), illustrating the hydrogen bonding network and the N···N short contacts. Thermal ellipsoids at 50 % probability.

Table 7.2: Hydrogen bonds present in 2-(3-azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**).

D–H···A	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	∠(D–H···A) / °
N1–H1···O1	0.92(2)	2.17(2)	2.709(1)	116(1)
N1–H1···O1^{i}	0.92(2)	2.01(2)	2.867(1)	154(1)
O2–H4···O3^{ii}	0.97(2)	1.62(2)	2.587(1)	174(1)
O3–H5···N3^{iii}	0.90(2)	1.98(2)	2.881(1)	177(2)
O3–H6···N2^{iv}	0.86(2)	2.02(2)	2.872(1)	175(2)

Symmetry codes: (i) $-x+2, -y, -z$, (ii) $x, -y+0.5, z-0.5$, (iii) $x+1, y, z$, (iv) $-x+2, y+0.5, -z+0.5$.

7.2.3 NMR Spectroscopy

3-Azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) shows three signals for its three hydrogen atoms in the ^{1}H NMR spectrum in DMSO-d_6. The ring attached hydrogen atom is quite acidic with a shift of 14.96 ppm, interestingly emitting a very sharp signal (almost all acidic protons in this thesis show a very broad signal in DMSO-d_6). The two hydrogen atoms of the amide nitrogen are chemically not equal with shifts of 8.18 and 7.97 ppm, indicating a strong intramolecular hydrogen bond which prevents a rotation of the amine at room temperature and below. All three carbon atoms are observable in the ^{13}C NMR spectrum with signals at 157.5, 157.1 and 149.9 ppm. Additionally the ^{14}N NMR spectrum shows the broad signal of the azide beta nitrogen atom with a shift of −138 ppm.

2-(3-Azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**) shows only the signal of the methylene group at 3.73 ppm in the ^{1}H NMR spectrum, also in DMSO-d_6. Again all atoms are observable in the ^{13}C NMR spectrum. The carbon atoms of the triazole ring show shifts of 156.4 and 151.8 ppm, the carboxylic acid is at 169.5 ppm and the methylene group at 32.8 ppm. The azide beta nitrogen atom displays a usual shift of −135 ppm in the ^{14}N NMR spectrum.

The NMR shifts of the other neutral compounds are in accord with reported values.

7.2.4 Thermal Stabilities

The thermal stabilities of the investigated neutral azide containing triazoles and their metal salts were determined by DSC and DTA measurements.

Most of the compounds exhibit a rather moderate thermal stability and only two decompose above 180 °C, namely 5,5′-diazido-3,3′-bis(1*H*-1,2,4-triazole) (**53**) at 181 °C and 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) at 202 °C. The other neutral compounds with hydrogen (**50**), amine (**57**), nitrimine (**58**) and methyl (**64**) as second substituent decompose between 131 and 156 °C. Not surprisingly the highly energetic nitrimine derivative **58** displays the lowest thermal stability, while the methyl derivative **64** is the most stable.

Salt formation however flips this around. The least stable of the neutral compounds (**58**) is the only case in which the salts exhibit a higher thermal stability. The silver salt **59** begins to decompose at 141 °C and the potassium salt **60** at 142 °C. In all other cases the silver salts show much lower thermal stabilities than their corresponding neutral parent molecules. Interestingly, especially the silver salts of the two most stable neutral compounds **53** and **61** are much less thermally stable (**54**: 148 °C; **61**: 132 °C). As already mentioned, it was unfortunately not possible to obtain elemental analysis pure samples of the silver salts of 5-amino-3-azido-1*H*-1,2,4-triazole (**57**) and 3-azido-5-methyl-1*H*-1,2,4-triazole (**64**). A discussion of their thermal stabilities is therefore not feasible.

These results seem to confirm the observations from the previous chapters that energetic, electron withdrawing groups like nitro, cyano and nitrimino likely result in a less thermally stable neutral azido-1,2,4-triazole compound, but the salts improve upon the thermal stability. Less energetic and especially electron donating (or neutral) groups apparently can't stabilize the anion in its salts, thus they become less thermally stable than the neutral compounds.

7.2.5 Sensitivities and Energetic Properties

With very few exceptions most of the prepared compounds are very sensitive to impact, with values between 1 and 5 J. While most neutral compounds are only sensitive to friction (FS > 160 N), with the exception of 5,5′-diazido-3,3′-bis(1*H*-1,2,4-triazole) (**53**) and particularly 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**) with 48 and 7 N, respectively, the silver salts have all except for one to be classified as extremely sensitive, with values around 5 N. Curiously, the exception is the silver salt **59** of the nitrimine **58**, which is only very sensitive (20 N). The only compound which can be classified as completely insensitive is 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**).

All of the metal salts were tested for their capability of being a primary explosive. Thus, about 5 mg of substance was heated on a spatula by a lighter, and no direct flame contact, in the usual manner. The silver salts **51**, **54** and **59** of 3-azido-1*H*-1,2,4-triazole (**50**), 5,5′-diazido-3,3′-bis(1*H*-1,2,4-triazole) (**53**) and 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**), respectively, all detonated violently. Additionally both the diamminecopper(II) salt **55** of **53** and the potassium salt **60** of **58** were capable of a detonation. The silver (**62**) and copper (**63**) salts of 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) were not capable of a DDT. It should be mentioned that the isolated, but not clearly identified, products of the reaction of 5-amino-3-azido-1*H*-1,2,4-triazole (**57**) and 3-azido-5-methyl-1*H*-1,2,4-triazole (**64**) with silver nitrate were also both able to undergo a DDT upon heating. Compounds **51**, **54**, **55**, **59** and **60** can therefore be classified as primary explosives. All compounds, except

Table 7.3: Energetic properties of selected compounds.

Compound	IS / J	FS / N	ESD / mJ	T_d / °C	DDT	fast heating
50	4	192	200	139	—	—
51	1	5	12	129	yes	detonation
53	3	48	40	181	—	—
54	1	5	12	148	yes	detonation
55	1	10	—	122	yes	—
57	5	192	100	131	—	—
58	2	7	40	121	—	—
59	1	20	30	141	yes	detonation
60	5	144	80	142	yes	deflagration
61	40	360	100	202	—	—
62	5	40	15	132	no	deflagration
63	40	288	50	159	no	deflagration
64	40	160	1000	156	—	—

the diamminecopper(II) salt **55**, were further subjected to rapid heating by a preheated needle, while fixed onto a metal plate with transparent tape. In this case only the silver salts **51**, **54** and **59** were capable of a detonation. The alleged silver salts of **57** and **64** were also only deflagrating, similar to **60**, **62** and **63**.

7.2.6 Theoretical Calculations

The enthalpies of formation of the neutral compounds **50**, **53**, **57**, **58**, **61** and **64** were calculated at the CBS-4M level of theory, as described in chapter 1. All of the compounds are highly endothermic, with enthalpies of formation between 229.1 $\mathrm{kJ\,mol^{-1}}$ (**61**) and 975.5 $\mathrm{kJ\,mol^{-1}}$ (**53**). Table 11.1 in the summary (chapter 11) contains the calculated enthalpies of formation for the all investigated neutral compounds of this chapter and the previous chapters 2–6.

7.3 Conclusions

The goal of this chapter has been the characterization of several, and except for two (**61** and **66**), already reported azido-1,2,4-triazoles with different substituents on the second carbon atom concerning their capability to form primary explosives. The chosen substituents were hydrogen (**50**), a second 5-azido-1*H*-1,2,4-triazole (**53**), amine (**57**), nitrimine (**58**), carboxamide (**61**) and methyl (**64**). The neutral compounds mostly exhibit a rather moderate thermal stability in the vicinity of 140 °C. The novel compound 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) on the other hand decomposes at 202 °C, which is the best thermal stability of all neutral azidotriazoles described in the study at hand. Except for **61** and **64**, all of the neutral compounds have to be classified as highly sensitive to impact and friction. The calculated enthalpies of formation additionally prove the neutral compounds predominantly as highly endothermic. This results in silver salts which are all, again except for one (**62**), true primary explosives which undergo a DDT upon slow as well as, in the majority of cases, also upon rapid heating. Unfortunately, the silver salts are in every case, except for 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**), less thermally stable than the parent neutral molecule. An explanation might be that the electron withdrawing effect of the nitrimine can help to stabilize the anion, similar to 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) and 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**). The other compounds feature either electron donating or neutral groups.

7.4 Experimental Part

3-Azido-1*H*-1,2,4-triazole (50)

Sodium nitrite (8.26 g, 120 mmol) in water (10 mL) was added drop wise to 5-amino-1*H*-1,2,4-triazole (10.1 g, 120 mmol) in sulfuric acid (20 %, 125 mL) at 0 °C and stirred for 30 minutes. To this was added urea (2 g), followed drop wise by sodium azide (10.0 g, 154 mmol) in water (80 mL), then stirred for one hour at room temperature. The reaction mixture was neutralized with sodium hydrogen carbonate and extracted with ethyl acetate (4 × 100 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was suspended in toluene, evaporated again and washed with *n*-pentane to yield a colorless solid (11.5 g, 104 mmol, 87 %). ^{1}H NMR (DMSO-d_6): δ = 13.95 (s, NH), 8.42 (s, CH). ^{13}C NMR (DMSO-d_6): δ = 157.7, 145.3. ^{14}N NMR (DMSO-d_6): δ = −136 (N_β), −167. IR (ATR): $\tilde{\nu}$ = 3151 (w), 3047 (w), 2982 (w), 2891 (m), 2744 (m), 2423 (w), 2389 (w), 2241 (w), 2141 (vs), 1757 (w), 1693 (w), 1533 (w), 1509 (s), 1485 (m), 1451 (vs), 1366 (), 1330 (vs), 1284 (s), 1258 (s), 1219 (m), 1174 (vs), 1088 (s), 1013 (s), 979 (s), 845 (s), 794 (m), 786 (m), 733 (s), 629 (vs) cm^{-1}. MS (DEI+): m/z = 110.1 ([M]$^{+}$). EA ($C_2H_2N_6$): calculated C 21.82, H 1.83, N 76.35 %; found C 22.42, H 1.93, N 75.89 %. DSC (5 °C min^{-1}): T_m = 113 °C; T_d = 139 °C. Sensitivities (grain size < 100 µm): IS 4 J, FS 192 N, ESD 200 mJ.

Silver 3-azido-1,2,4-triazolate (51)

Silver nitrate (170 mg, 1.00 mmol) in water (20 mL) was added drop wise to **50** (110 mg, 1.00 mmol) in water (20 mL) at 80 °C and the resulting suspension was refluxed in the dark for 30 minutes. After cooling down the precipitate was filtered off and washed with water, ethanol and diethyl ether to yield a pale yellow solid (153 mg, 7.05 µmol, 71 %). IR (ATR): $\tilde{\nu}$ = 3128 (w), 2421 (w), 2239 (w), 2123 (vs), 1493 (vs), 1474 (s), 1460 (s), 1437 (s), 1389 (m), 1368 (m), 1322 (w), 1282 (w), 1236 (m), 1193 (m), 1181 (m), 1073 (w), 1046 (m), 998 (w), 885 (w), 867 (w), 856 (w), 775 (w), 710 (m), 673 (w), 666 (w), 658 (w) cm^{-1}. EA (C_2HAgN_6): calculated C 11.07, H 0.46, N 38.74 %; found C 11.10, H 0.75, N 37.06 %. DSC (5 °C min^{-1}): T_d = 125 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 5 N, ESD 12 mJ.

5,5′-Diamino-3,3′-bis(1*H*-1,2,4-triazole) (52)

Oxalic acid dihydrate (20.0 g, 159 mmol) and aminoguanidinium hydrogen carbonate (45.4 g, 332 mmol) were suspended in water (250 mL) and dissolved with concentrated hydrochloric acid (60 mL), then refluxed for one hour. The solvent was evaporated under reduced pressure and the residue was dissolved in water (250 mL). The pH was adjusted to 14 with sodium hydroxide and the solution was refluxed for one hour. Acetic acid (30 mL) was added drop wise, the resulting precipitate was filtered off, washed with large amounts of water and suspended in water (1.2 L). This (filtration, washing, suspending) was repeated two more times to remove unreacted oxalic acid. The third suspension was adjusted to pH 14 with sodium hydroxide, then acidified with acetic acid (40 mL). The resulting precipitate was filtered off, washed with water and ethanol, then suspended in ethanol (600 mL) and stirred overnight to yield a colorless solid (8.83 g, 53.1 mmol, 67 %) after filtration. IR (ATR): $\tilde{\nu}$ = 3304 (m), 3169 (m), 3063 (m), 2979 (m), 2921 (m), 2841 (m), 2761 (m), 2708 (m), 1640 (vs), 1606 (vs), 1487 (vs), 1447 (m), 1434 (m), 1371 (m), 1258 (s), 1244 (vs), 1138 (w), 1106 (s), 1095 (s), 1059 (s), 1049 (s), 983 (m), 973 (m), 806 (m), 733 (vs), 663 (s) cm^{-1}. MS (DEI+): m/z = 166.1 ($[M]^+$). EA ($C_4H_6N_8$): calculated C 28.92, H 3.64, N 67.44 %; found C 28.90, H 3.59, N 66.05 %.

5,5′-Diazido-3,3′-bis(1*H*-1,2,4-triazole) dihydrate (53)

Sodium nitrite (1.86 g, 27.0 mmol) was added in small portions to a suspension of **52** (1.50 g, 9.03 mmol) in sulfuric acid (25 %, 200 mL) at 0 °C, then stirred for three hours at room temperature. A small amount of urea was added, followed by sodium azide (11.7 g, 180 mmol) in small portions. The reaction mixture was refluxed for about 30 minutes, then extracted with ethyl acetate (4 × 80 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was recrystallized from boiling water to yield colorless, fluffy needles (1.57 g, 6.18 mmol, 68 %). IR (ATR): $\tilde{\nu}$ = 3370 (w), 3124 (w), 2995 (w), 2909 (w), 2854 (w), 2778 (w), 2693 (m), 2571 (m), 2525 (m), 2385 (m), 2236 (w), 2152 (s), 1882 (w), 1660 (m), 1610 (w), 1554 (vs), 1514 (m), 1473 (m), 1460 (s), 1426 (vs), 1342 (m), 1314 (w), 1268 (w), 1254 (s), 1217 (w), 1192 (vs), 1121 (w), 1051 (m), 1031 (s), 976 (s), 797 (s), 724 (vs), 684 (w), 615 (w), 606 (w) cm^{-1}. MS (DEI+): $m/z = 218.1$ ([M]$^+$). EA ($C_4H_2N_{12} \cdot 2\,H_2O$): calculated C 18.90, H 2.38, N 66.13 %; found C 19.20, H 2.41, N 66.31 %. DSC (5 °C min^{-1}): $T_d = 183$ °C.

Disilver 5,5′-diazido-3,3′-bis(1,2,4-triazolate) (54)

Silver nitrate (340 mg, 2.00 mmol) in water (20 mL) was added drop wise to **53** (254 mg, 1.00 mmol) in water (30 mL) at 80 °C and the resulting suspension was refluxed in the dark for 30 minutes. After cooling down the precipitate was filtered off and washed with water, ethanol and diethyl ether to yield a colorless solid (292 mg, 6.76 µmol, 68 %). IR (ATR): $\tilde{\nu} = 2159$ (vs), 1482 (vs), 1469 (vs), 1442 (s), 1290 (s), 1240 (s), 1130 (w), 1074 (w), 995 (w), 797 (w), 722 (s), 683 (w) cm^{-1}. EA ($C_4Ag_2N_{12}$): calculated C 11.12, N 38.92 %; found C 11.79, N 39.44 %. DSC (5 °C min^{-1}): $T_d = 148$ °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 5 N, ESD 12 mJ.

Diamminecopper(II) 5,5′-diazido-3,3′-bis(1,2,4-triazolate) (55)

Copper(II) nitrate trihydrate (121 mg, 0.50 mmol) in hot water (1 mL) was added to **53** (127 mg, 0.50 mmol) in hot aqueous ammonia solution (25 %, 5 mL). The blue precipitate was filtered off and washed with ethanol to yield a fine dark blue powder (122 mg, 389 µmol, 78 %). IR (ATR): $\tilde{\nu}$ =3366 (w), 3298 (w), 3215 (w), 3143 (w), 2442 (w), 2362 (w), 2340 (w), 2132 (vs), 1624 (m), 1494 (w), 1447 (vs), 1431 (vs), 1274 (m), 1224 (vs), 1144 (m), 1088 (w), 1034 (w), 986 (m), 788 (w), 720 (s), 668 (w) cm^{-1}. EA ($C_4H_6CuN_{14}$): calculated C 15.31, H 1.93, N 62.50 %; found C 15.99, H 1.90, N 62.06 %. DTA (5 °C min^{-1}): $T_d =$ 122 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 10 N.

5-Acetamido-3-azido-1*H*-1,2,4-triazole (56)

Sodium nitrite (1.52 g, 22.0 mmol) in a minimal amount of water was added drop wise to a suspension of **46** (2.84 g, 20.0 mmol) in sulfuric acid (25 %, 75 mL) at 0 °C. The resulting orange solution was stirred for one hour at room temperature, followed by the drop wise addition of sodium azide (1.63 g, 25.0 mmol) in a minimal amount of water at 0 °C. The resulting orange precipitate was filtered off after stirring for four hours at room temperature and washed with water, ethanol and *n*-pentane to yield a fine yellow-orange powder (1.84 g, 11.0 mmol, 55 %). ^{1}H NMR (DMSO-d_6): $\delta = 13.25$ (s, 1H, NH), 11.64 (s, 1H, NH), 2.08 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): $\delta = 154.3$, 148.7. ^{14}N NMR (DMSO-d_6): $\delta = -134$ (N_β). IR (ATR): $\tilde{\nu} = 3262$ (m), 3215 (m), 3116 (w), 3058 (m), 2946 (m), 2836 (w), 2432 (w), 2344 (w), 2232 (w), 2141 (vs), 1698 (vs), 1609 (s), 1559 (s), 1500 (s), 1435 (vs), 1376 (s), 1360 (s), 1263 (s), 1240 (vs), 1226 (vs), 1119 (s), 1072 (s), 1032 (w), 1010 (s), 819 (m), 801 (m), 775 (s), 723 (vs), 668 (s) cm^{-1}. MS (DEI+): $m/z = 167.2$ ([M]$^+$). EA ($C_4H_5N_7O$): calculated C 28.75, H 3.02, N 58.67 %; found C 28.25, H 3.20, N 59.58 %. DSC (5 °C min^{-1}): $T_d = 212$ °C. Sensitivities (grain size < 100 µm): IS 25 J, FS 240 N, ESD 300 mJ.

5-Amino-3-azido-1*H*-1,2,4-triazole (57)

Compound **56** (5.00 g, 29.9 mmol) was stirred in hydrochloric acid (10 %, 100 mL) for five hours at 100 °C. The reaction mixture was neutralized with sodium hydrogen carbonate, filtered and extracted with ethyl acetate (4 × 100 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was washed with *n*-pentane to yield a yellow solid (1.75 g, 14.0 mmol, 47 %). ^{1}H NMR (DMSO-d_6): $\delta = 11.84$ (s, 1H, NH), 6.27 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): $\delta = 157.1$, 154.2. ^{14}N NMR (DMSO-d_6): $\delta = -135$ (N_β). IR (ATR): $\tilde{\nu} = 3419$ (m), 3397 (m), 3333 (w), 3126 (m), 2994 (m), 2948 (m), 2807 (w), 2764 (w), 2438 (w), 2246 (w), 2145 (vs), 1667 (vs), 1600 (m), 1542 (vs), 1458 (m), 1407 (s), 1368 (m), 1223 (vs), 1106 (s), 1072 (m), 1019 (m), 828 (w), 764 (w), 716 (s) cm^{-1}. MS (DEI+): $m/z = 125.2$ ([M]$^+$). EA ($C_2H_3N_7$): calculated C 19.20, H 2.42, N 78.86 %; found C 19.95, H 2.85, N 76.86 %. DSC (5 °C min^{-1}): $T_d = 131$ °C. Sensitivities (grain size < 100 µm): IS 5 J, FS 192 N, ESD 100 mJ.

3-Azido-5-nitrimino-1,4*H*-1,2,4-triazole (58)

Nitric acid (65 %, 3 mL) was added over the course of 30 minutes to **57** (1.00 g, 7.99 mmol) in sulfuric acid (98 %, 3 mL) at 5 °C. The reaction mixture was stirred for 30 minutes at that temperature and for one hour without cooling, then poured on ice (100 g). The yellow solution was extracted with ethyl acetate (3 × 50 mL) and the combined organic phases were dried over magnesium sulfate. The solvent was evaporated under reduced pressure and the residue was washed with *n*-pentane to yield a pale yellow solid (1.00 g, 5.88 mmol, 74 %). ^{1}H NMR (DMSO-d_6): $\delta = 4.62$ (br). ^{13}C NMR (DMSO-d_6): $\delta = 150.8$, 149.8. ^{14}N NMR (DMSO-d_6): $\delta = -20$ (NO_2), -139 (N_β). IR (ATR): $\tilde{\nu} = 3183$ (w), 2967 (w), 2864 (w), 2618 (w), 2372 (w), 2312 (w), 2190 (m), 2158 (s), 1764 (w), 1591 (vs), 1559 (m), 1494 (s), 1416 (m), 1301 (vs), 1252 (vs), 1187 (s), 1116 (s), 1095 (vs), 1012 (m), 993 (s), 862 (w), 852 (w), 806 (w), 783 (w), 768 (m), 748 (m), 679 (vs) cm^{-1}. Raman: $\tilde{\nu} = 2156$ (3), 1607 (11), 1585 (7), 1559 (100), 1442 (4), 1318 (2), 1191 (5), 1118 (6), 1020 (26), 996 (14), 855 (4), 784 (3), 751 (6) cm^{-1}. MS (DEI+): $m/z = 169.8$ ([M]$^+$). EA ($C_2H_2N_8O_2$): calculated C 14.12, H 1.19, N 65.88 %; found C 14.43, H 1.43, N 63.56 %. DSC (5 °C min^{-1}): $T_d = 134$ °C. Sensitivities (grain size < 100 µm): IS 2 J, FS 7 N, ESD 40 mJ.

Silver 3-azido-5-nitrimino-1*H*-1,2,4-triazolate (59)

Silver nitrate (170 mg, 1.00 mmol) in water (20 mL) was added drop wise to **58** (170 mg, 1.00 mmol) in water (20 mL) at 80 °C and the resulting suspension was refluxed in the dark for 30 minutes. After cooling down the precipitate was filtered off and washed with water, ethanol and diethyl ether to yield a pale brown solid (184 mg, 6.64 µmol, 66 %). IR (ATR): $\tilde{\nu}$ = 3388 (w), 3055 (w), 2455 (w), 2235 (w), 2146 (s), 1626 (w), 1544 (m), 1525 (s), 1479 (s), 1429 (m), 1380 (m), 1335 (w), 1295 (s), 1262 (s), 1228 (vs), 1126 (m), 1113 (s), 1039 (m), 1003 (m), 892 (m), 800 (m), 787 (m), 770 (m), 727 (vs), 678 (m) cm^{-1}. EA ($C_2HAgN_8O_2$): calculated C 8.67, H 0.36, N 40.46 %; found C 8.69, H 1.18, N 37.95 %. DSC (5 °C min^{-1}): T_d = 141 °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 20 N, ESD 30 mJ.

Potassium 3-azido-5-nitrimino-1*H*-1,2,4-triazolate (60)

Potassium carbonate (138 mg, 1.00 mmol) and **58** (342 mg, 2.00 mmol) were refluxed in a mixture of water (20 mL) and ethanol (20 mL) for one hour. The solvent was evaporated under reduced pressure to yield a yellow powder (363 mg, 1.74 mmol, 87 %). ^{13}C NMR (DMSO-d_6): δ = 157.0, 154.2. ^{14}N NMR (DMSO-d_6): δ = −11 (NO_2), −135 (N_β). IR (ATR): $\tilde{\nu}$ = 3609 (w), 3350 (w), 3177 (w), 2441 (w), 2247 (w), 2143 (s), 1642 (w), 1597 (w), 1526 (m), 1509 (s), 1435 (s), 1404 (s), 1383 (s), 1343 (vs), 1255 (s), 1229 (s), 1135 (m), 1088 (s), 1002 (s), 857 (m), 832 (w), 801 (w), 785 (w), 765 (m), 739 (m), 732 (m), 701 (w), 687 (w) cm^{-1}. MS (FAB+): m/z = 38.9 ($[K]^+$). MS (FAB−): m/z = 169.4 ($[C_2HN_8O_2]^-$). EA ($C_2HKN_8O_2$): calculated C 11.54, H 0.48, N 53.83 %; found C 11.38, H 1.51, N 49.91 %. DSC (5 °C min^{-1}): T_d = 142 °C. Sensitivities (grain size < 100 µm): IS 5 J, FS 144 N, ESD 80 mJ.

3-Azido-1*H*-1,2,4-triazole-5-carboxamide (61)

Sodium nitrite (826 mg, 12.0 mmol) in water (2 mL) was added drop wise to a suspension of **13** (1.53 g, 12.0 mmol) in sulfuric acid (20 %, 25 mL) at 0 °C. The suspension was stirred for 30 minutes at 0 °C, after which a small amount of urea was added followed by drop wise addition of sodium azide (1.00 g, 15.4 mmol) in water (8 mL). After stirring the suspension for 75 minutes at room temperature the colorless precipitate was filtered off and washed with ethanol. The filtrate was extracted with ethyl acetate (3 × 15 mL), the combined organic phases were washed with water (2 × 10 mL), dried over magnesium sulfate and evaporated under reduced pressure. The colorless residue was combined with the precipitate and recrystallized from boiling water to yield a colorless powder (930 mg, 6.07 mmol, 51 %). ^{1}H NMR (DMSO-d_6): δ = 14.96 (s, 1H, NH), 8.18 (s, 1H, NH_2), 7.97 (s, 1H, NH_2). ^{13}C NMR (DMSO-d_6): δ = 157.5, 157.1, 149.9. ^{14}N NMR (DMSO-d_6): δ = −138 (N_β). IR

(ATR): $\tilde{\nu}$ = 3473 (w), 3358 (w), 3301 (m), 3178 (m), 2819 (m), 2239 (w), 2145 (s), 1699 (vs), 1668 (s), 1587 (m), 1487 (vs), 1455 (vs), 1327 (s), 1212 (s), 1158 (m), 1107 (m), 1035 (s), 1010 (m), 842 (w), 791 (w), 765 (w), 734 (m), 722 (m), 692 (m), 672 (w) cm^{-1}. Raman (300 mW): $\tilde{\nu}$ = 2173 (18), 2144 (4), 1693 (5), 1591 (16), 1546 (11), 1513 (100), 1491 (42), 1453 (9), 1335 (17), 1229 (5), 1157 (21), 1100 (27), 1035 (42), 1012 (7), 792 (7) cm^{-1}. MS (DEI+): m/z = 153.2 ([M]$^+$). EA ($C_3H_3N_7O$): calculated C 23.53, H 1.98, N 64.04 %; found C 23.98, H 2.08, N 63.76 %. DTA (5 °C min^{-1}): T_d = 202 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 100 mJ.

Silver 3-azido-1,2,4-triazolate-5-carboxamide (62)

Silver nitrate (170 mg, 1.00 mmol) in water (10 mL) was added drop wise to **53** (254 mg, 1.00 mmol) in hot water (30 mL) and the resulting suspension was stirred in the dark for 30 minutes. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a colorless powder (200 mg, 769 µmol, 77 %). IR (ATR): $\tilde{\nu}$ = 3468 (m), 3340 (m), 2445 (w), 2151 (vs), 2052 (w), 1679 (vs), 1591 (vs), 1486 (m), 1472 (s), 1459 (vs), 1361 (w), 1304 (m), 1230 (s), 1122 (m), 1089 (w), 832 (w), 716 (m), 700 (s), 669 (m) cm^{-1}. MS (DEI+): m/z = 107.0 ([Ag]$^+$). EA ($C_3H_2AgN_7O$): calculated C 13.86, H 0.78, N 37.72 %; found C 13.78, H 0.86, N 37.54 %. DTA (5 °C min^{-1}): T_d = 132 °C. Sensitivities (grain size < 100 µm): IS 5 J, FS 40 N, ESD 15 mJ.

Copper(II) bis(3-azido-1,2,4-triazolate-5-carboxamide) monohydrate (63)

Copper sulfate pentahydrate (125 mg, 500 µmol) in water (10 mL) was added to **61** (153 mg, 1.00 mmol) in hot water (20 mL) after the addition of sodium hydroxide solution (2 M, 0.5 mL, 1.0 mmol). At instant a green precipitate was formed and the suspension was stirred for 30 minutes, then filtered. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a lime green powder (157 mg, 407 µmol, 81 %). IR (ATR): $\tilde{\nu}$ = 3444 (w), 3201 (w), 2461 (w), 266 (w), 2142 (vs), 2057 (w), 1674 (s), 1610 (m), 1537 (w), 1502 (w), 1470 (vs), 1444 (vs), 1379 (w), 1338 (m), 1320 (m), 1240 (m), 1233 (m), 1147 (m), 1123 (w), 1097 (w), 1079 (w), 741 (m) cm^{-1}. EA ($C_6H_4CuN_{14}O_4 \cdot H_2O$): calculated C 18.68, H 1.57, N 50.83 %; found C 19.43, H 1.68, N 50.19 °C. DTA (5 °C min^{-1}): T_d = 159 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 288 N, ESD 50 mJ.

3-Azido-5-methyl-1*H*-1,2,4-triazole (64)

Triaminoguanidinium chloride (10.5 g, 75.0 mmol) was refluxed in acetic acid (175 mL) for eight hours. Concentrated hydrochloric acid (125 mL) was added and refluxed for ten more minutes. The solvent was then evaporated under reduced pressure. The residue was, after suspension in toluene and repeated evaporation, dissolved in water (125 mL) and slowly added to a solution of sodium nitrite (11.4 g, 165 mmol) in water (15 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at room temperature, neutralized with sodium hydrogen carbonate and extracted with diethyl ether (3 × 100 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure to yield a yellow solid (5.92 g, 47.7 mmol, 64 %). ^{1}H NMR (DMSO-d_6): $\delta = 13.55$ (s, 1H, NH), 2.31 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): $\delta = 156.6, 154.0, 11.8$. ^{14}N NMR (DMSO-$d_6$): $\delta = -135$ (N_β). IR (ATR): $\tilde{\nu} = 3335$ (w), 3163 (w), 3032 (w), 2925 (w), 2782 (m), 2680 (m), 2434 (m), 2367 (w), 2244 (w), 2137 (vs), 1764 (w), 1593 (w), 1549 (w), 1500 (m), 1442 (s), 1415 (vs), 1399 (vs), 1382 (s), 1372 (vs), 1316 (s), 1221 (s), 1150 (m), 1062 (vs), 1042 (s), 894 (s), 835 (w), 798 (s), 728 (s), 711 (s) cm^{-1}. MS (DEI+): $m/z = 124.1$ ([M]$^+$). EA ($C_3H_2N_{10}$): calculated C 29.03, H 3.25, N 67.72 %; found C 29.38, H 3.17, N 66.94 %. DSC (5 °C min^{-1}): $T_m = 136$ °C; $T_d = 156$ °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 160 N, ESD 1000 mJ.

2-(3-Amino-1*H*-1,2,4-triazol-5-yl)acetic acid (65)

Concentrated hydrochloric acid (42 mL) was carefully added drop wise to a mixture of malonic acid (45.9 g, 441 mmol) and aminoguanidinium hydrogen carbonate (60.0 g, 441 mmol), then stirred for 70 minutes at 70 °C. The clear solution was cooled to room temperature, neutralized with sodium hydroxide solution (6.1 M, 185 mL) and stirred for one hour at 95 °C. The suspension was allowed to cool to room temperature, filtered, acidified with hydrochloric acid (12 %) to pH 2–3 and stored in the fridge overnight. The precipitate was filtered off, suspended in water (350 mL) and refluxed for five minutes, then filtered off again, washed with water and dried at 120 °C to yield a colorless powder (28.0 g, 197 mmol, 45 %). ^{1}H NMR (DMSO-d_6): $\delta = 5.77$ (br, CH_2). ^{13}C NMR (DMSO-d_6): $\delta = 171.0, 157.9, 154.0, 34.5$. IR (ATR): $\tilde{\nu} = 3344$ (w), 3112 (w), 2690 (w), 1669 (vs), 1635 (s), 1597 (s), 1571 (s), 1456 (w), 1414 (m), 1374 (s), 1278 (m), 1255 (m), 1193 (w), 1100 (w), 1002 (s), 934 (w), 919 (s), 826 (m), 754 (w), 687 (s) cm^{-1}. MS (DEI+): $m/z = 142.0$ ([M]$^+$). EA ($C_4H_6N_4O_2$): calculated C 33.81, H 4.26, N 39.42 %; found C 33.74, H 4.16, N 39.24 %.

2-(3-Azido-1*H*-1,2,4-triazol-5-yl)acetic acid (66)

Sodium nitrite (2.07 g, 30.0 mmol) was added to **65** (2.84 g, 20.0 mmol) in sulfuric acid (20 %, 200 mL) at 0 °C and stirred for 10 minutes. A small amount of urea was added, followed by sodium azide (2.60 g, 40.0 mmol), then stirred for four hours at room temperature. The red suspension was extracted with ethyl acetate (4 × 100 mL), the combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was suspended in toluene, evaporated again and washed with *n*-pentane to yield a pale yellow solid (630 mg, 3.75 mmol, 19 %). ^{1}H NMR (DMSO-d_6): $\delta = 3.73$ (s, CH_2). ^{13}C NMR (DMSO-d_6): $\delta = 169.5, 156.4, 151.8, 32.8$. ^{14}N NMR (DMSO-$d_6$): $\delta = -135$ (N_β). MS (DEI+): $m/z = 168.2$ ($[M]^+$).

5-(5-Azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole

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manuscripts in preparation

8.1 Introduction

Chapters 2–7 dealt with various derivatives of azido-1,2,4-triazole as potential primary explosive forming compounds. Another option would be the utilization of a 1,2,3-triazole due to its higher enthalpy of formation (272 kJ mol^{-1}) owing to the three catenated nitrogen atoms,[184] instead of the two in 1,2,4-triazole (109 kJ mol^{-1}).[54] Due to the protracted synthesis (eleven steps) of 5-azido-4-nitro-2*H*-1,2,3-triazole,[185] and the experiences with the thermal stability of the azido-1,2,4-triazoles, it was concluded that the most worthwhile compound would be 5-(5-azido-2*H*-1,2,3-triazol-4-yl)tetrazole (**72**). Carrying a C-C linked tetrazole ring as second substituent could provide similar benefits to the salts of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) if the tetrazole ring has a higher acidity than the azido-1,2,3-triazole. A suitable precursor in the form of 5-amino-1-benzyl-1,2,3-triazole-4-carbonitrile (**69**) had already been reported in 1956,[186] but no further studies could be found.

The goal of this study has therefore been the synthesis of the novel 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**71**) and its derivatives with azido (**72**) and nitro (**73**) groups, their comprehensive characterization, the capability of **72** to form primary explosives and the comparison of the compounds with the respective 1,2,4-triazole isomers and analogues.

8.2 Results and Discussion

8.2.1 Syntheses

There are two possible routes to the intermediate 5-amino-1-benzyl-1,2,3-triazole-4-carbonitrile (**69**). The first one is the direct synthesis from benzyl azide (**67**) and malononitrile with sodium in ethanol,[186] but this reaction suffers from low yields and the formation of a byproduct (5-amino-l-benzyl-4-carbiminoethoxy-1,2,3-triazole), due to the presence of the second nitrile which can react with the formed ethoxide. The second option is the well working synthesis (80 %) of 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**68**) from benzyl azide (**67**) and cyanoacetamide with sodium in ethanol,[186] which can then be further processed in two different ways. The first one would be the debenzylation to

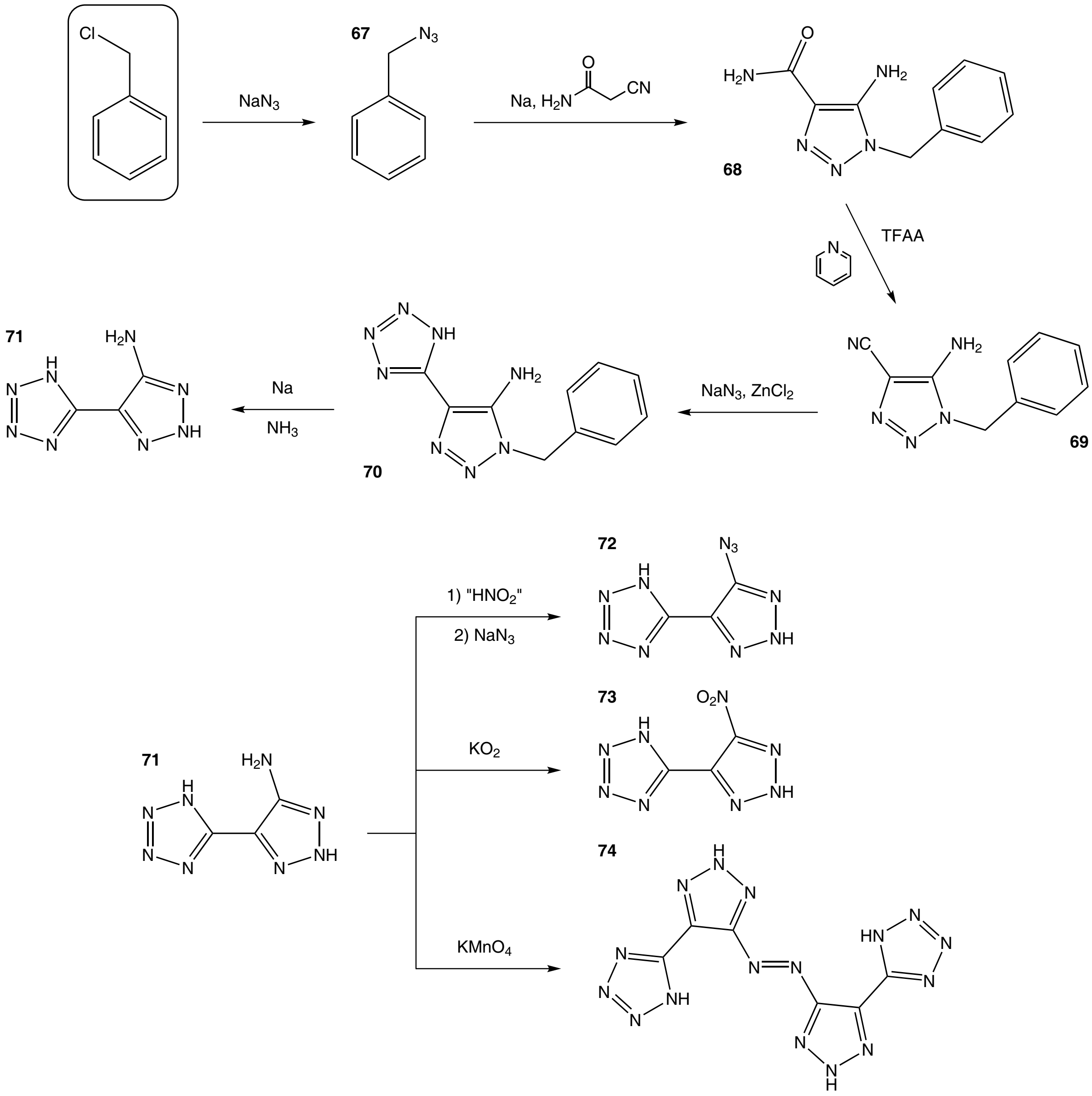
4-amino-2*H*-1,2,3-triazole-5-carboxamide with sodium in liquid ammonia,[186] followed by the dehydration of the amide to a nitrile. Although the debenzylation is working well (96 %), the dehydration did not result in a complete conversion with various reagents (phosphorus pentoxide, phosphoryl chloride, phosphorus pentachloride, thionyl chloride). Therefore the benzyl protective group was left on the triazole and thus enabling the use of trifluoroacetic anhydride by protecting the ring from its acylation properties, resulting in a complete conversion of **68** into **69** in high yields (86 %). The next step, the formation of 5-(5-amino-1-benzyl-1,2,3-triazol-4-yl)tetrazole (**70**) from **69** and sodium azide, proved to be quite difficult due to the frequent hydrolysis of the nitrile, in addition to the desired product, when zinc chloride was employed in a protic solvent (water, ethanol, methanol). Hydrochloric acid and ammonium chloride in the same solvents did not result in partial hydrolysis, but also did not yield any product, and neither did acetic acid (both as acid and as solvent). Utilization of the polar, aprotic tetrahydrofuran and zinc chloride finally yielded pure **70** (97 %). Debenzylation was again carried out with sodium in liquid ammonia to obtain the title compound 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**71**) in high yield (95 %). The optimized route is shown in scheme 8.1.

The amine of **71** was then converted into different energetic moieties, as illustrated in scheme 8.1. The azido derivative **72** was obtained in high yield (87 %) by diazotation with sodium nitrite in sulfuric acid, followed by a diazo azide exchange with sodium azide. The nitro derivative **73** could not be obtained by the common reaction with an excess of sodium nitrite in sulfuric acid, a method which works well with 5-(5-amino-1*H*-1,2,4-triazol-3-yl)tetrazole for example,[139] but it was obtained by oxidation of the amine with potassium superoxide in tetrahydrofuran in a fair yield (68 %). Azo coupling with potassium permanganate in water yielded 1,2-bis(4-(1*H*-tetrazol-5-yl)-2*H*-1,2,3-triazol-5-yl)diazene (**74**) in also only a fair yield (48 %).

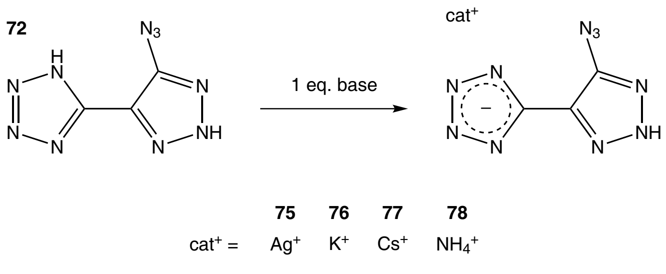
The alkali metal salts with potassium (**76**) and cesium (**77**), as well as the nitrogen-rich salt with ammonium (**78**) were prepared according to scheme 8.2 in aqueous or ethanolic solution using **72** and the corresponding carbonates or free base and subsequent slow evaporation of the solvent at room temperature or under reduced pressure. The silver salt **75** was prepared by the reaction of **72** with silver nitrate in water. A guanidinium salt was also tried but it was not possible to obtain a pure product.

8.2.2 Crystal Structure Analysis

Unfortunately, only the precursor molecule 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**68**) yielded suitable single crystals for X-ray diffraction and none of the main compounds **71**–**74**. It crystallized in the monoclinic space group $P2_1/c$ with four formula units per



Scheme 8.1: Synthetic route towards 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**71**) from commercially available benzyl azide, and its energetic derivatives 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**72**), 5-(5-nitro-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**73**) and 1,2-bis(4-(1*H*-tetrazol-5-yl)-2*H*-1,2,3-triazol-5-yl)diazene (**74**).



Scheme 8.2: Synthesis of the energetic salts **75**–**78** of 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**72**).

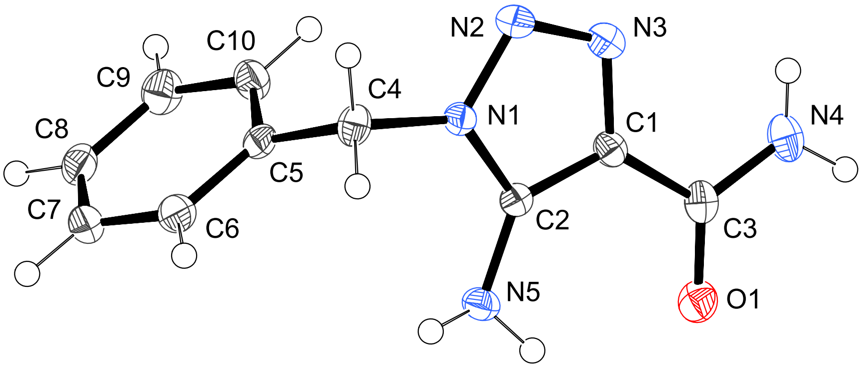


Figure 8.1: Molecular structure of 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**68**). Thermal ellipsoids at 50 % probability.

unit cell. The molecular unit is depicted in figure 8.1. The bond lengths of the 1,2,3-triazole ring are between the length of the corresponding single and double bonds,[100] with the N1–N2 bond being significantly longer (1.376(1) Å) than the N2–N3 bond (1.304(1) Å), which is quite common for 1,4,5-substituted 1,2,3-triazoles.[187–190] The bond lengths of the amino group attached to the triazole (1.351(2) Å), as well as the amide N4–C3 bond (1.346(2) Å) are considerably shorter than the corresponding single bonds, caused by an involvement of the non-bonding electron pair of the nitrogen atoms, with both groups being almost planar. The amide group and the triazole ring are practically in plane (C2–C1–C3–O1: 1.66(2)°). The molecule features one weak and undirected intramolecular hydrogen bond between the ring amine and the amide oxygen as N5–H3···O1 (D···A: 2.956(1) Å; D–H···A: 125(1)°), and a long but directed intermolecular hydrogen bond N4–H2···O1^{i} (D···A: 3.070(2) Å; D–H···A: 171(2)°) resulting in dimers (see figure 8.2 for both). The dimers are connected by undulated ribbons through a π-π stacking interaction of the phenyl groups, depicted in figure 8.2. The distance between the two aromatic moieties is 3.531(2) Å, which is characteristic for these interactions.[191] The second intermolecular interaction which connects the ribbons is formed by a very long but directed hydrogen bond N5–H4···N2^{ii} between the amino moiety and a nitrogen atom of a neighboring triazole (D···A: 3.128(2) Å; D–H···A: 164(1)°), slightly above the sum of the van der Waals radii ($\sum r_\mathrm{w}$(N,N) = 3.10 Å).[104] The resulting crystal structure, presented in figure 8.3, has two areas which are either dominated by polar hydrogen bonds or by nonpolar π-π stacking interactions. The parameters of the described hydrogen bonds are summarized in table 8.1.

8.2.3 NMR Spectroscopy

All compounds prepared herein were investigated by multinuclear NMR spectroscopy (^{1}H and ^{13}C, some additionally ^{14}N and ^{15}N). ^{13}C NMR spectroscopy is well suited to differentiate between the precursor molecules **68**–**70**, the title compound **71** and its further derivatives

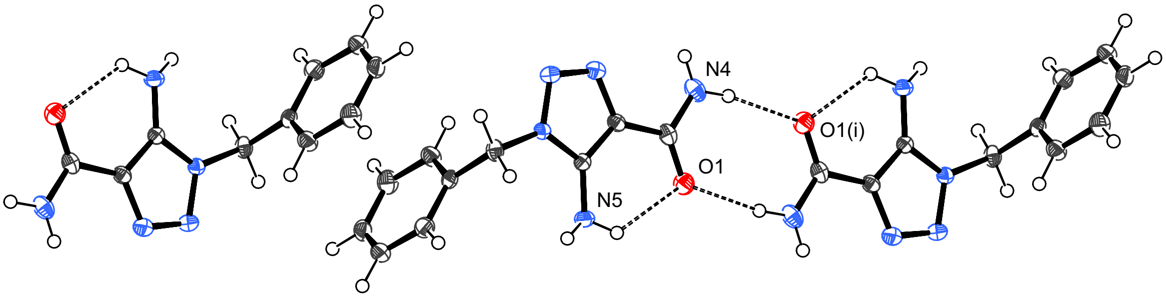


Figure 8.2: Hydrogen bonds and π-π stacking interactions of 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**68**). Thermal ellipsoids at 50 % probability. Symmetry code: (i) $-x+1, -y+3, -z+1$.

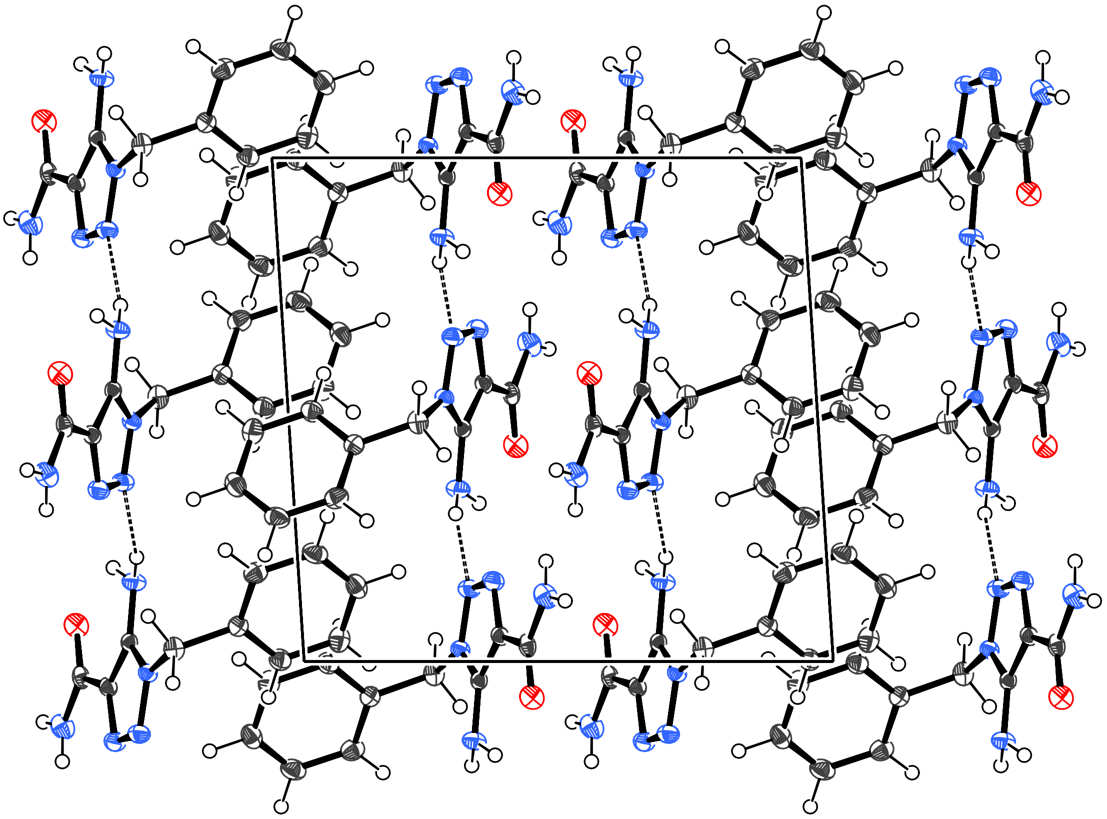


Figure 8.3: Unit cell of 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**68**) along the (010) axis, illustrating the intermolecular N5–H4· · · N2^{ii} hydrogen bond. Thermal ellipsoids at 50 % probability.

Table 8.1: Hydrogen bonds present in 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**68**).

D–H· · · A	d(D–H) / Å	d(H· · · A) / Å	d(D· · · A) / Å	∠(D–H· · · A) / °
N5–H3· · · O1	0.88(2)	2.36(1)	2.956(1)	125(1)
N4–H2· · · O1^{i}	0.90(2)	2.17(2)	3.070(2)	171(2)
N5–H4· · · N2^{ii}	0.91(2)	2.24(2)	3.128(2)	164(1)

Symmetry codes: (i) $-x+1, -y+3, -z+1$; (ii) $x, -y+1.5, z-0.5$.

72–**74**. While **68**–**70** all show the signals of the benzyl group (phenyl: 135.2–136.0, 128.7, 127.8–127.9, 127.4–127.5 ppm; methylene: 48.4–48.8 ppm), those are completely gone in the spectrum of **71**. The signal of the triazole carbon atom attached to the exocyclic carbon is at 121.8 (**68**), 113.7 (**69**) and 114.4 ppm (**70**). The carbon atom carrying the amine shows a signal at 144.9 (**68**), 148.0 (**69**) and 148.6 ppm (**70**). While the spectrum of **68** shows a signal at 164.5 ppm, stemming from the amide, **69** has the signal of the nitrile at 101.3 ppm and shows no signs of the former. Pure **70** finally exhibits a new signal at 142.9 ppm, belonging to the newly formed tetrazole. The signals of compounds **71**–**74** (^{1}H, ^{13}C and ^{14}N) are compiled in table 8.2. While **72**–**74** show three sharp signals for the two triazole and one tetrazole carbon atoms in their corresponding ^{13}C NMR spectra, **71** shows only one sharp signal at 149.0 ppm, attributed to the tetrazole, and two small and broad signals at 147.6 and 111.6 ppm, attributed to the triazole. The corresponding ^{14}N NMR spectra show the signals of the central azide nitrogen atom (N_β) of **72** at −138 ppm as a broad signal and the nitro group of **73** at −21 ppm. Compounds **72** and **73** were further investigated by ^{15}N and ^{15}N{^{1}H} NMR spectroscopy. Both the proton coupled and decoupled spectra are depicted in figure 8.4. All nitrogen atoms display clearly visible resonances in the ^{15}N NMR spectra of both **72** (eight signals) and **73** (six signals). The tetrazole emits only two signals due to the enabled proton exchange in DMSO-d_6, equalizing the four nitrogen atoms to one protonated (−101.9 ppm in **72**, −65.4 ppm in **73**) and one non-protonated (−11.1 ppm in **72**, −14.4 ppm in **73**), similar to 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole and 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)-2*H*-tetrazole for example.[139] The triazole shows three signals in both compounds, with one being strong and sharp (−74.1 ppm in **72**, −51.1 ppm in **73**) and the other two being weaker and broad (−55.7 and −126.3 ppm in **72**, −65.4 and −97.2 ppm in **73**). The ^{15}N{^{1}H} NMR spectra confirm that the signals at −126.3 and −97.2 ppm carry the proton, in addition to their high field shift. The signal of the protonated nitrogen atom of the tetrazole ring is in all spectra broader than that of the triazole. The remaining signals are belonging to the azide (−143.2, −148.6 and −303.3 ppm) of **72** and the nitro group (−27.5 ppm) of **73**. While the signal at −303.3 ppm in the spectrum of **72** can be clearly attributed to the alpha nitrogen atom of the azide, the signals at −143.2 and −148.6 ppm have nearly identical intensities and are thus preventing a clear assignment to the beta and gamma nitrogen atoms, similar to **49**. Deprotonation only marginally affects the carbon atom shifts in **76**–**78**, indicating a fast proton exchange between the two rings and the basic solvent. The ^{14}N NMR spectra show, in addition to the central azide nitrogen atom (N_β) of the anion at −135 to −136 ppm, two smaller and rather broad signals around 20 and −44 ppm for **76** and **77**. The only signal observable in the ^{14}N NMR spectrum of **78** is that of the ammonium cation at −353 ppm.

Table 8.2: NMR signals of **71**–**74** and **76**–**78** in DMSO-d_6 at room temperature.

	δ			
	^{1}H	^{13}C (triazole)	^{13}C (tetrazole)	^{14}N
71	16.19$^{\text{i}}$, 14.64$^{\text{i}}$, 6.03$^{\text{ii}}$	147.6, 111.6	149.0	—
72	15.81$^{\text{i}}$	147.7, 123.0	143.1	−138$^{\text{iii}}$
73	9.93$^{\text{i}}$	151.1, 127.7	147.7	−21$^{\text{iv}}$
74	10.09$^{\text{i}}$	153.7, 126.6	147.2	—
76	5.60$^{\text{vi}}$	150.8, 123.7	139.5	25$^{\text{vi}}$, −42$^{\text{vi}}$, −136$^{\text{iii}}$
77	—	150.7, 123.6	139.5	20$^{\text{vi}}$, −44$^{\text{vi}}$, −135$^{\text{iii}}$
78	8.09$^{\text{vi}}$, 7.42$^{\text{vi}}$	150.0, 123.6	140.8	−135$^{\text{iii}}$, −353$^{\text{v}}$

(i) aromatic NH; (ii) NH_2; (iii) azide N_β; (iv) NO_2; (v) NH_4^+; (vi) clear assignment not possible.

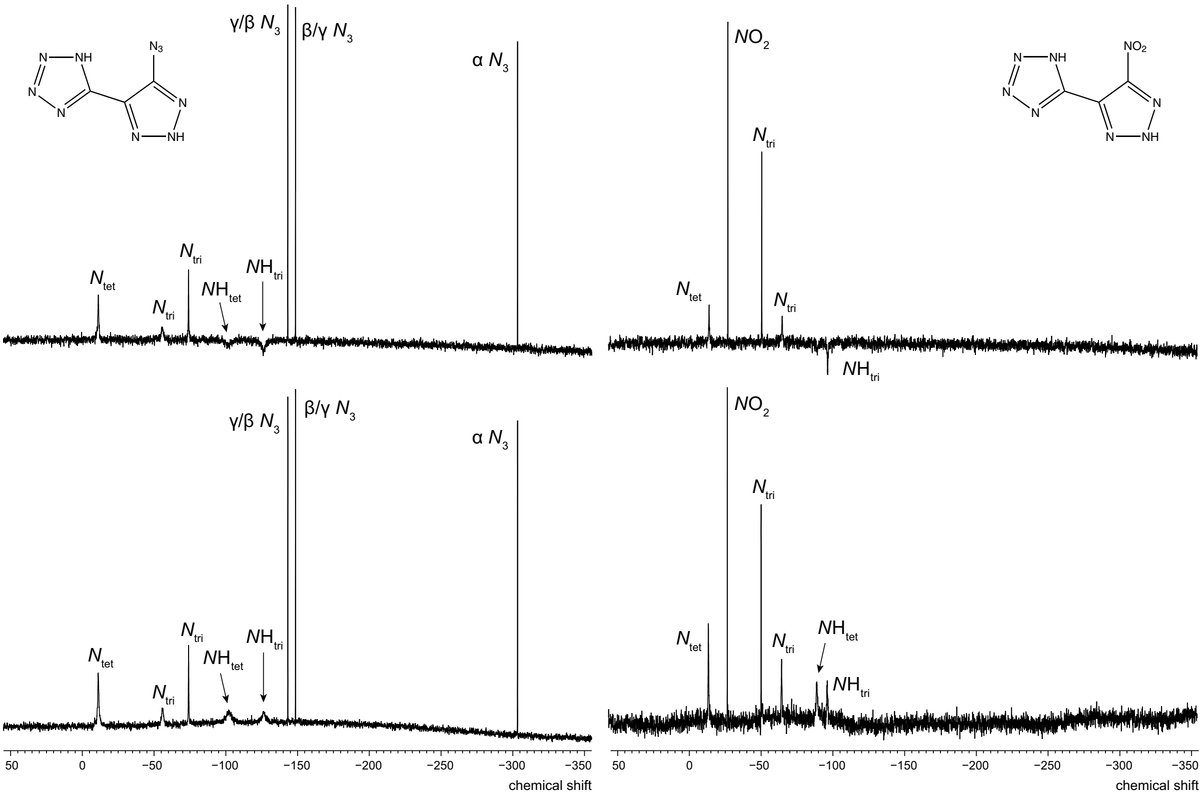


Figure 8.4: ^{15}N and ^{15}N{^{1}H} NMR spectra of 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**72**) and 5-(5-nitro-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**73**) in DMSO-d_6 at room temperature.

8.2.4 Thermal Stabilities

The thermal behavior of the synthesized compounds was investigated by differential thermal analysis (DTA). The amino derivative **71** displays, as expected, the highest thermal stability of the neutral compounds (241 °C), while the nitro derivative **73** (188 °C), azido derivative **72** (152 °C) and especially the diazene bridged derivative **74** (128 °C) are significantly less thermally stable. It is interesting to note that, while the isomer 5-(5-amino-1*H*-1,2,4-triazol-3-yl)tetrazole (347 °C) and its nitro derivative (211 °C) display higher thermal stabilities than **71** and **73**,[139] respectively, due to the 1,2,4-triazole, the azido derivative **33** exhibits the same decomposition temperature as **72**, as does the third isomer **49**. Unfortunately, salt formation does not raise the thermal stability, contrary to the monovalent salts of **33** (and **20**). The potassium (**76**), cesium (**77**), silver (**75**) and ammonium (**78**) salts of **72** are all less thermally stable than the neutral compound, with decomposition temperatures between 121 and 148 °C. Unfortunately, it was not possible to obtain suitable single crystals for X-ray diffraction, thus it is unknown which site is deprotonated in the solid state. While the nitrogen-rich salts of **71** all feature a deprotonated tetrazole ring,[192] those of **73** feature a deprotonated triazole ring.[193] Nevertheless, most of the nitrogen-rich salts of both compounds are still less thermally stable than the corresponding neutral compounds.

8.2.5 Sensitivities

The parent compound **71** is the least sensitive of the neutral compounds, although it is still sensitive to impact (10 J), but insensitive to friction (360 N). While the azido derivative **72** is very sensitive to impact (3 J) and friction (10 N), the nitro derivative **73** is only sensitive to impact (4 J) and friction (108 N). Interestingly, the diazene **74** is very sensitive to both impact (2 J) and friction (28 N), although it is a dihydrate and proper dehydration proved unsuccessful. 5-(5-Amino-1*H*-1,2,4-triazol-3-yl)tetrazole and its derivatives show the same trends, although the amine itself is additionally insensitive to friction, while its nitro derivative displays likewise lower sensitivities (25 J, 288 N) than its isomer **73**.[139] The metal salts of **72** are all very sensitive to impact (1 J and less) and extremely sensitive to friction (less than 5 N). Especially the silver salt **75** is an extremely dangerous compound and can be detonated by the slightest amount of friction when dry. The potassium salt **76** tends to attract moisture from the air and thus becomes less sensitive (2 J, 60 N). The ammonium salt on the other hand is comparatively insensitive (20 J, 360 N). The cesium salt **77** displays a high sensitivity to electrostatic discharge (14 mJ), in the range of primary explosives like lead azide (5 mJ), while the potassium salt **76** is somewhat less sensitive (40 mJ). The ammonium salt **78** on the other hand is one of the least sensitive of all compounds described in the study at hand (1000 mJ). The sensitivity of the silver

Table 8.3: Energetic properties of 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**72**) and its metal salts **75**–**77**.

Compound	IS / J	FS / N	ESD / mJ	T_d / °C	DDT	fast heating
72	3	10	250	152	—	—
75	1	$\lll 5$	—	121	yes	detonation
76	2	60	40	135	yes	detonation
77	1	5	14	148	yes	detonation

Figure 8.5: Copper tube test of **77**. Top: type A igniter; left: empty copper tube; middle: damaged copper tube after deflagration of pure **77** (100 mg); right: remnants after detonation (300 mg RDX, 50 mg **77**).

salt **75** was not determined due to its extreme friction sensitivity. The metal salts always detonated (impact, friction and electrostatic discharge), while the nitrogen-rich salt merely only vanished without sound.

8.2.6 Energetic Properties

All three metal salts are true primary explosives and detonated when heated slowly on a spatula, when poked by a hot needle, and even when burned, although the potassium salt **76** lost its capability to detonate upon rapid heating or burning after a while, due to the partial hydration in air. The cesium salt **77** was therefore tested for its capability to initiate a commonly used secondary explosive. RDX was loaded in a copper tube (6.50 mm × 57.70 mm), layered with **77** and slightly pressed. For the ignition, a commercial type A electrical igniter was used on top,[109] with a direct contact to the primary explosive. Both 50 and 25 mg of **77** were able to initiate 300 mg of RDX, resulting in the destruction of the copper tube. A test with only 100 mg of **77** and no RDX resulted in a deflagration. Figure 8.5 illustrates the results of this preliminary performance test.

The enthalpies of formation of **71**–**73** and RDX were calculated at the CBS-4M level

Table 8.4: Energetic properties and detonation parameters of **71**–**73** and RDX.

	71	**72**	**73**	RDX
Formula	$C_3H_4N_8$	$C_3H_2N_{10}$	$C_3H_2N_8O_2$	$C_6H_5N_7O_4$
M / g mol^{-1}	152.13	178.13	182.11	222.12
IS / J	10	3	4	7.4
FS / N	>360	10	108	120
ESD / mJ	800	250	250	200
N / %	73.66	78.64	61.53	37.84
$-\Omega$ / %	84.1	60.0	43.9	21.6
T_d / °C	241	152	188	204
ρ / g cm^{-3} [a]	1.66	1.56	1.69	1.80
$\Delta_f H°_{(s)}$ / kJ mol^{-1} [b]	460	846	516	85
$\Delta_f U°_{(s)}$ / kJ kg^{-1} [c]	3120	4833	2915	481
Calculated detonation parameters (EXPLO5 6.02)				
$-Q_v$ / kJ kg^{-1}	3481	4929	5064	5903
T_{ex} / K	2479	3678	3816	3849
p_{CJ} / kbar	237	220	263	347
D / m s^{-1}	8397	7963	8251	8854
V_0 / L mol^{-1}	772	758	753	785

[a] Room temperature density; [b] calculated solid state enthalpy of formation; [c] calculated solid state energy of formation.

of theory (table 8.4), as described in chapter 1. Calculations with the various isomers regarding the position of the proton revealed the 1*H*-tetrazole to be the most stable, albeit the difference to the 2*H*-tetrazole is only marginally. Detonation parameters of the neutral compounds were calculated with EXPLO5 6.02.[194] The program is based on the steady-state model of equilibrium and uses the Becker–Kistiakowsky–Wilson equation of state (BKW EOS) for gaseous detonation products and the Murnaghan EOS for both solid and liquid products. The parameters of the BKW EOS in EXPLO5 6.02 are calibrated particularly for the formation of nitrogen gas, which is the main detonation product for compounds with a high nitrogen content. It is designed to enable the calculation of detonation parameters at the Chapman–Jouguet point. The calculations were performed using the maximum densities at room temperature, measured with a helium pycnometer. The calculated detonation performances of **71**–**73** and RDX are summarized in table 8.4. The calculated detonation velocities range from 7963 m s^{-1} (**72**) up to 8397 m s^{-1} (**71**). The calculated detonation pressures are in the range of 237 to 263 kbar and the volume of gaseous reaction products amounts up to 772 L kg^{-1} (**71**).

8.3 Conclusions

The main goal of this study has been the preparation and thorough characterization of the novel compound 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**72**). Unfortunately, its molecular structure in the solid state could not be determined. Although **72** features a 1,2,3-triazole, its decomposition temperature (152 °C) is identical to the 1,2,4-triazole isomers **33** and **49**. While **72** is, according to UN standards, very sensitive to impact and friction, similar to **33** and **49**, its ammonium salt **78** displays much lower sensitivities. The metal salts with potassium (**76**), cesium (**77**) and silver (**75**) are all true primary explosives and capable of a fast DDT when heated slowly on a spatula, when poked by a hot needle and when burned. The silver salt **75** is an extremely friction sensitive compound and should be handled with utmost care. The salts are more potent primary explosives than those of **33** and its hydroxy derivative **20**, due to their capability to detonate even when burned. The initiation capability of the cesium salt **77** was thus demonstrated with RDX in a copper tube with a commercial igniter. Unfortunately, all salts are even less thermally stable than the parent compound, thereby limiting a practical application. Additionally, the detonation parameters of **71**–**73** were calculated using EXPLO5, revealing the compounds as inferior to RDX (mainly due to low densities).

8.4 Experimental Part

Benzyl azide (67)

Benzyl chloride (106 g, 840 mmol) and sodium azide (82.0 g, 1.26 mol) were stirred in a mixture of ethanol (400 mL) and water (50 mL) for 20 hours at 95 °C. The suspension was afterwards poured in water (2 L), divided into four portions and each was extracted with diethyl ether (2 × 200 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure at 50 °C to obtain a clear, yellow liquid (106 g, 796 mmol, 95 %). ^{1}H NMR (DMSO-d_6): $\delta = 7.44$–7.34 (m, 5H, CH), 4.44 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6): $\delta = 135.6$, 128.7, 128.4, 128.1, 53.6 (CH_2). ^{14}N NMR (DMSO-d_6): $\delta = -127$ (N_β), -164 (N_γ), -300 (N_α).

5-Amino-1-benzyl-1,2,3-triazole-4-carboxamide (68)

Cyanoacetamide (16.8 g, 200 mmol) and **67** (26.6 g, 200 mmol) were added to sodium (4.60 g, 200 mmol) in ethanol (500 mL) and the mixture was refluxed for one hour. The precipitate was filtered off and washed with water and ethanol, then suspended in ethanol/water (4:1, 500 mL) and heated for half an hour. The precipitate was filtered off again, and washed with water, ethanol and diethyl ether to yield a colorless solid (34.5 g, 159 mmol, 80 %). ^{1}H

NMR (DMSO-d_6): δ = 7.50 (br, 2H, NH_2), 7.39–7.20 (m, 5H, CH), 5.45 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ = 164.5 ($CONH_2$), 144.9 (C_{tri}), 136.0, 128.7, 127.8, 127.4, 121.8 (C_{tri}), 48.4 (CH_2). MS (DEI+): m/z = 217.2 ($[M]^+$). EA ($C_{10}H_{11}N_5O$): calculated C 55.29, H 5.10, N 32.24 %; found C 55.17, H 4.93, N 32.11 %.

5-Amino-1-benzyl-1,2,3-triazole-4-carbonitrile (69)

Trifluoroacetic anhydride (26.0 mL, 184 mmol) was carefully added to a suspension of **68** (20.0 g, 92.1 mmol) in dry pyridine (210 mL), while cooled with an ice/water bath. The flask was sealed and the deep red solution was stirred for 16 hours without removing or refreshing the cooling bath. The reaction mixture was poured on ice (250 g) and stirred for about 24 hours at room temperature. Concentrated hydrochloric acid (220 mL) was added drop wise, then stirred for about 48 hours at room temperature until a completely homogenized, light brown suspension was obtained. The precipitate was filtered off, washed with diluted hydrochloric acid and water, then suspended in toluene and stirred for one hour. The solvent was evaporated under reduced pressure and the residue was suspended in *n*-pentane, filtered off and washed with *n*-pentane to yield a pale brownish powder (15.7 g, 78.8 mmol, 86 %). ^1H NMR (DMSO-d_6): δ = 7.40–7.30 (m, 3H, CH), 7.25–7.23 (m, 2H, CH), 7.18 (s, 2H, NH_2), 5.43 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ = 148.0 (C_{tri}), 135.2, 128.7, 127.9, 127.5, 113.7 (C_{tri}), 101.3 (CN), 48.8 (CH_2). MS (DEI+): m/z = 199.1 ($[M]^+$). EA ($C_{10}H_9N_5$): calculated C 60.29, H 4.55, N 35.16 %; found C 60.29, H 4.47, N 34.97 %.

5-(5-Amino-1-benzyl-1,2,3-triazol-4-yl)tetrazole (70)

A suspension of **69** (15.9 g, 80.0 mmol), sodium azide (10.4 g, 160 mmol) and zinc chloride (13.6 g, 100 mmol) in dry tetrahydrofuran (250 mL) was stirred for 16 hours at 70 °C. Concentrated hydrochloric acid (14 mL) was added to the cooled down solution, which was then stirred for half an hour. The solvent was evaporated under reduced pressure and the residue was suspended in half concentrated hydrochloric acid (300 mL) and stirred for several hours. The precipitate was filtered off and washed with diluted hydrochloric acid and water to yield a pale yellow powder (18.8 g, 77.6 mmol, 97 %). ^1H NMR (DMSO-d_6): δ = 7.37–7.26 (m, 5H, CH), 6.61 (s, 2H, NH_2), 5.55 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ = 148.6 (C_{tri}), 142.9 (C_{tet}), 135.8, 128.7, 127.9, 127.5, 114.4 (C_{tri}), 48.8 (CH_2). MS (DEI+): m/z = 242.2 ($[M]^+$). EA ($C_{10}H_{10}N_8$): calculated C 49.58, H 4.16, N 46.26 %; found C 48.95, H 4.05, N 45.32 %.

5-(5-Amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (71)

Sodium was added in small pieces to a clear red solution of **70** (37.6 g, 155 mmol) in liquid ammonia (about 150 mL) until a deep blue suspension was obtained, carefully followed by the addition of ammonium chloride until the blue color was completely gone. The solvent was allowed to slowly evaporate and the residue was dissolved in water (about 200 mL), then filtered. The filtrate was evaporated under reduced pressure and the residue was dissolved again in water (200 mL), then acidified with concentrated hydrochloric acid (40 mL). The precipitate was filtered off and washed with water to yield a yellow powder (22.5 g, 148 mmol, 95 %). ^{1}H NMR (DMSO-d_6): δ = 16.19 and 14.64 (br, 2H, NH), 6.03 (br, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ = 149.0 (C_{tet}), 147.6 (br, C_{tri}), 111.6 (br, C_{tri}). IR (ATR): $\tilde{\nu}$ = 3437 (m), 3317 (m), 3227 (w), 3138 (m), 3036 (m), 2976 (m), 2895 (m), 2796 (m), 2700 (m), 2553 (m), 1624 (vs), 1564 (s), 1503 (m), 1467 (m), 1404 (w), 1372 (m), 1332 (w), 1250 (w), 1240 (s), 1214 (m), 1185 (m), 1145 (m), 1090 (s), 1019 (m), 1003 (s), 971 (vs), 866 (vs), 764 (m), 749 (vs), 691 (m) cm^{-1}. Raman (300 mW): $\tilde{\nu}$ = 1646 (24), 1627 (100), 1571 (8), 1474 (5), 1406 (21), 1250 (8), 1178 (6), 1151 (9), 1104 (13), 1020 (23), 747 (9), 421 (12), 334 (15), 172 (14), 140 (24), 121 (31), 63 (10) cm^{-1}. MS (DEI+): m/z = 152.1 ([M]$^+$). EA ($C_3H_4N_8$): calculated C 23.69, H 2.65, N 73.66 %; found C 24.07, H 2.76, N 73.29 %. DTA (5 °C min^{-1}): T_d = 235 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 360 N, ESD 800 mJ.

5-(5-Azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (72)

Sodium nitrite (2.07 g, 30.0 mmol) was added to a suspension of **71** (3.04 g, 20.0 mmol) in sulfuric acid (20 %, 200 mL) at 0 °C. The cooling was removed and the yellow reaction mixture was stirred for three hours at room temperature. Sodium azide (2.60 g, 40.0 mmol) was then added in small portions and stirred for 30 minutes at room temperature. The resulting colorless foamy suspension was refluxed until a clear solution was obtained. The resulting suspension after cooling down was extracted with ethyl acetate (4 × 150 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was suspended in toluene, evaporated again and washed with *n*-pentane to yield a colorless solid (3.08 g, 17.3 mmol, 87 %). ^{1}H NMR (DMSO-d_6): δ = 15.81 (br). ^{13}C NMR (DMSO-d_6): δ = 147.7 (C_{tri}), 143.1 (C_{tet}), 123.0 (C_{tri}). ^{14}N NMR (DMSO-d_6): δ = −138 (N_β). ^{15}N NMR (DMSO-d_6): δ = −11.1 (N_{tet}), −55.7 (N_{tri}), −74.1 (N_{tri}), −101.9 (NH_{tet}), −126.3 (NH_{tri}), −143.2 (N_γ/N_β), −148.6 (N_β/N_γ), −303.3 (N_α). IR (ATR): $\tilde{\nu}$ = 3524 (w), 3227 (w), 3132 (w), 2923 (w), 2800 (w), 2677 (w), 2426 (w), 2331 (w), 2147 (vs), 1915 (w), 1628 (s), 1525 (vs), 1407 (w), 1356 (w), 1345 (w), 1322 (m), 1308 (w), 1295 (w), 1250 (w), 1209 (s), 1160 (w), 1121 (w), 1103 (w), 1067 (m), 1019 (s), 1006 (m), 977 (s), 835 (m), 795 (m), 769 (m), 757 (s), 717 (w), 703 (w), 694 (w) cm^{-1}. Raman (300 mW): 2163 (12), 1631 (100), 1534 (22), 1445 (5), 1409 (17), 1357 (18), 1326 (9), 1299 (5), 1252 (8), 1219 (11), 1168 (17), 1126 (5), 1022 (16), 978 (9), 797 (6), 760 (11) cm^{-1}. MS (DEI+): $m/z = 178.1$ ($[M]^+$). EA ($C_3H_2N_{10}$): calculated C 20.23, H 1.13, N 78.64 %; found C 19.83, H 1.89, N 73.11 %. DTA ($5\,°C\,min^{-1}$): $T_d = 152\,°C$. Sensitivities (grain size $< 100\,\mu m$): IS 3 J, FS 10 N, ESD 250 mJ.

5-(5-Nitro-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (73)

Potassium superoxide (4.75 g, 66.9 mmol) and **71** (1.00 g, 6.57 mmol) were stirred in tetrahydrofuran (50 mL) for 72 hours at 60 °C. The solvent was evaporated under reduced pressure and ice (80 g) was added to the dry residue, followed by sulfuric acid (98 %, 11 mL). The resulting yellow suspension was stirred for one hour, then extracted with methyl ethyl ketone (5 × 75 mL). The combined organic phases were washed with a saturated sodium chloride solution (2 × 50 mL), dried over magnesium sulfate and evaporated under reduced pressure. The resulting green solid was dried in fine vacuum overnight, pestled, resuspended in dichloromethane, sonicated for a few minutes and filtered off to yield a pale green solid (814 mg, 4.47 mmol, 68 %). ^1H NMR (DMSO-d_6): $\delta = 9.93$ (br). ^{13}C NMR (DMSO-d_6): $\delta = 151.1$ (C_{tri}), 147.7 (C_{tet}), 127.7 (C_{tri}). ^{14}N NMR (DMSO-d_6): $\delta = -21$ (NO_2). ^{15}N NMR (DMSO-d_6): $\delta = -14.4$ (N_{tet}), -27.5 (NO_2), -51.1 (N_{tri}), -65.4 (N_{tri}), -89.6 (NH_{tet}), -97.2 (NH_{tri}). IR (ATR): $\tilde{\nu} = 3221$ (w), 3113 (w), 3055 (w), 2908 (w), 1630 (w), 1547 (vs), 1500 (vw), 1472 (w), 1383 (s), 1350 (m), 1244 (w), 1197 (vw), 1138 (m), 1097 (m), 1065 (s), 1021 (w), 1008 (s), 991 (m) 845 (m), 835 (vs), 744 (m), 726 (m), 707 (m) cm^{-1}. Raman (300 mW): $\tilde{\nu} = 1652$ (12), 1630 (100), 1546 (6), 1470 (16), 1414 (7), 1387 (23), 1340 (23), 1284 (8), 1244 (6), 1201 (7), 1014 (11), 987 (8), 833 (5), 504 (7), 383 (5), 166 (5), 137 (9), 92 (40), 79 (24) cm^{-1}. MS (DEI+): $m/z = 182.2$ ($[M]^+$), 30.1 ($[NO]^+$). EA ($C_3H_2N_8O_2$): calculated C 19.79, H 1.11, N 61.53 %; found C 19.88, H 1.63, N 59.98 %. DTA ($5\,°C\,min^{-1}$): $T_m = 180\,°C$, $T_d = 188\,°C$. Sensitivities (grain size $< 100\,\mu m$): IS 4 J, FS 108 N, ESD 250 mJ.

1,2-Bis(4-(1*H*-tetrazol-5-yl)-2*H*-1,2,3-triazol-5-yl)diazene dihydrate (74)

Potassium permanganate (1.05 g, 6.67 mmol) was added in small portions to **71** (1.52 g, 10.0 mmol) in aqueous sodium hydroxide (10 %, 40 mL) at 70 °C. After stirring for two hours at 100 °C, ethanol (10 mL) was added and stirred for further 15 minutes. The suspension was filtered through kieselgur and washed until the filtrate was colorless. The combined filtrates were evaporated under reduced pressure, the residue was suspended in hydrochloric acid (2 M, 100 mL) and stirred for several hours. The precipitate was filtered off and washed with diluted hydrochloric acid and water to yield a yellow solid (700 mg, 2.08 mmol, 42 %). ^{1}H NMR (DMSO-d_6): $\delta = 10.09$ (br). ^{13}C NMR (DMSO-d_6): $\delta = 153.7$ (C_{tri}), 147.2 (C_{tet}), 126.6 (C_{tri}). IR (ATR): $\tilde{\nu} = 3522$ (w), 3422 (w), 3232 (s), 2824 (w), 2748 (w), 2613 (w), 2501 (m), 2360 (m), 2000 (vw), 1877 (w), 1637 (m), 1611 (m), 1498 (m), 1428 (vw), 1406 (m), 1369 (s), 1344 (m), 1298 (vw), 1245(w), 1220 (w), 1207 (w), 1178 (w), 1143 (w), 1125 (vs), 1076 (vs), 1030 (vs), 1004 (s), 977 (s), 960 (s), 903 (m), 822 (vs), 772 (w), 726 (m), 672 (vw) cm^{-1}. Raman (300 mW): $\tilde{\nu} = 1638$ (37), 1613 (16), 1503 (16), 1492 (17), 1469 (100), 1432 (21), 1404 (8), 1369 (56), 1344 (69), 1329 (31), 1298 (10), 1245 (7), 1200 (14), 1182 (5), 1151 (4), 1125 (6), 980 (14), 903 (8), 621 (7), 353 (4) cm^{-1}. MS (FAB−): $m/z = 299.1$ ($[M]^+$). EA ($C_3H_4N_8 \cdot 2\,H_2O$): calculated C 21.43, H 2.40, N 66.65 %; found C 22.68, H 2.32, N 66.07 %. DTA (5 °C min^{-1}): $T_d = 128$ °C. Sensitivities (grain size < 100 µm): IS 2 J, FS 28 N, ESD 700 mJ.

Silver 5-(5-azido-2*H*-1,2,3-triazol-4-yl)tetrazolate (75)

Silver nitrate (85 mg, 0.50 mmol) in water (20 mL) was added drop wise to **72** (89 mg, 0.50 mmol) in water (20 mL) at 80 °C and the resulting suspension was refluxed in the dark for 30 minutes. After cooling down the precipitate was filtered off and washed with water, ethanol and diethyl ether to yield a pale yellow solid. The yield was not determined due to the extremely high friction sensitivity. DTA (5 °C min^{-1}): $T_d = 121$ °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS $\lll$ 5 N.

Potassium 5-(5-azido-2*H*-1,2,3-triazol-4-yl)tetrazolate (76)

Potassium carbonate (138 mg, 1.00 mmol) and **72** (356 mg, 2.00 mmol) were refluxed in water (30 mL) for 30 minutes. The solvent was left to evaporate and the yellow residue was dried in fine vacuum to yield a yellow solid (341 mg, 1.58 mmol, 79 %). ^{1}H NMR (DMSO-d_6): $\delta = 5.60$ (br). ^{13}C NMR (DMSO-d_6): $\delta = 150.8$ (C_{tri}), 139.5 (C_{tet}), 123.7 (C_{tri}). ^{14}N NMR (DMSO-d_6): $\delta = 25, -42, -136$ (N_β). IR (ATR): $\tilde{\nu} = 3361$ (w), 3053 (m), 2911 (m), 2868 (m), 2789 (m), 2157 (s), 2135 (vs), 1625 (m), 1604 (s), 1516 (vs), 1471 (s), 1386 (m), 1368 (m), 1316 (m), 1297 (m), 1235 (vs), 1203 (m), 1121 (s), 1026 (s), 976 (vs), 865 (m), 812 (w), 789 (m), 771 (m), 737 (w), 691 (w), 656 (w) cm^{-1}. MS (FAB+): $m/z = 39.0$ ($[K]^+$). MS (FAB−): $m/z = 177.2$ ($[C_3HN_{10}]^-$). EA (C_3HKN_{10}): calculated C 16.67, H 0.47, N 64.78 %; found C 15.87, H 1.51, N 53.93 %. DTA (5 °C min^{-1}): $T_d = 135$ °C. Sensitivities (grain size < 100 µm): IS 2 J, FS 60 N, ESD 40 mJ.

Cesium 5-(5-azido-2*H*-1,2,3-triazol-4-yl)tetrazolate (77)

Cesium carbonate (326 mg, 1.00 mmol) and **72** (356 mg, 2.00 mmol) were refluxed in water (30 mL) for 30 minutes. The solvent was left to evaporate and the yellow residue was dried in fine vacuum to yield a green-yellow solid (505 mg, 1.63 mmol, 82 %). ^{13}C NMR (DMSO-d_6): $\delta = 150.7$ (C_{tri}), 139.5 (C_{tet}), 123.6 (C_{tri}). ^{14}N NMR (DMSO-d_6): $\delta = 20, -44, -135$ (N_β). IR (ATR): $\tilde{\nu} = 3149$ (w), 2948 (w), 2811 (w), 2706 (w), 2483 (m), 2443 (m), 2411 (m), 2340 (m), 2248 (w), 2130 (vs), 1815 (m), 1755 (w), 1704 (w), 1595 (s), 1573 (m), 1537 (w), 1499 (s), 1489 (vs), 1429 (w), 1384 (m), 1365 (s), 1325 (w), 1295 (m), 1222 (vs), 1194 (vs), 1157 (m), 1132 (m), 1119 (s), 1075 (m), 1030 (m), 1016 (vs), 970 (vs), 939 (s), 848 (w), 821 (w), 798 (vs), 767 (s), 688 (w), 663 (w) cm^{-1}. MS (FAB+): $m/z = 133.1$ ([Cs]$^+$). MS (FAB−): $m/z = 177.2$ ($[C_3HN_{10}]^-$). EA (C_3HCsN_{10}): calculated C 11.62, H 0.33, N 45.18 %; found C 11.63, H 0.98, N 38.24 %. DTA (5 °C min^{-1}): $T_d = 148$ °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 5 N, ESD 14 mJ.

Ammonium 5-(5-azido-2*H*-1,2,3-triazol-4-yl)tetrazolate (78)

Aqueous ammonia solution (2 M, 1 mL, 2.00 mmol) and **72** (356 mg, 2.00 mmol) were refluxed in ethanol (20 mL) for 30 minutes. The solvent was evaporated under reduced pressure and the yellow residue was washed with a low amount of ethanol and diethyl ether, then dried in fine vacuum to yield a pale yellow solid (348 mg, 1.77 mmol, 80 %). ^{1}H NMR (DMSO-d_6): $\delta = 8.09$ (br), 7.42 (br). ^{13}C NMR (DMSO-d_6): $\delta = 150.0$ (C_{tri}), 140.8 (C_{tet}), 123.6 (C_{tri}). ^{14}N NMR (DMSO-d_6): $\delta = -135$ (N_β), -353 (NH_4^+). IR (ATR): $\tilde{\nu} = 3043$ (s), 2819 (s), 2366 (w), 2155 (vs), 1881 (w), 1705 (w), 1622 (m), 1604 (m), 1524 (s), 1505 (s), 1433 (vs), 1393 (m), 1372 (m), 1318 (m), 1301 (w), 1216 (s), 1167 (w), 1155 (w), 1132 (w), 1101 (w), 1031 (m), 980 (vs), 872 (w), 819 (w), 796 (s), 769 (m), 758 (w), 689 (w), 658 (w) cm^{-1}. MS (FAB+): $m/z = 18.1$ ($[NH_4]^+$). MS (FAB−): $m/z = 177.3$ ($[C_3HN_{10}]^-$). EA ($C_3H_5N_{11}$): calculated C 18.46, H 2.58, N 78.95 %; found C 18.64, H 2.86, N 72.88 %. DTA (5 °C min^{-1}): $T_d = 132$ °C. Sensitivities (grain size < 100 µm): IS 20 J, FS 360 N, ESD 1000 mJ.

5-(Tetrazol-1-yl)-2*H*-tetrazole

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9.1 Introduction

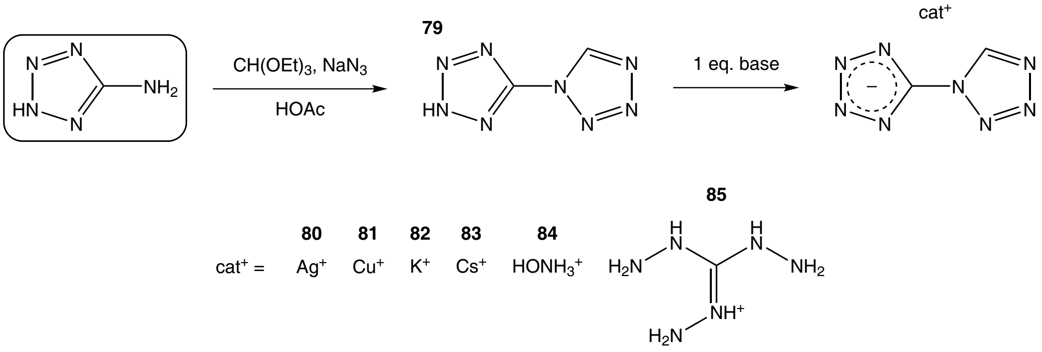
As already mentioned in the introductory chapter, most tetrazole derivatives had already been investigated as primary explosives over the course of the past century. A comparatively new simple tetrazole derivative is 5-(tetrazol-1-yl)-2*H*-tetrazole (1,5′-bistetrazole), one of the three bistetrazoles with the sum formula $C_2H_2N_8$ and first reported in 1985.[140] The other two possibilities are the currently unknown N-N bridged 1,1′-isomer and the C-C bridged 5,5′-isomer from 1914.[133] The latter has been extensively studied since, especially regarding nitrogen-rich and metal salts.[134,135,195–198] The anion of the base compound is not energetic enough to be suitable for ionic primary explosives,[198] but the potassium salt of the *N*-nitramine was recently reported as a potent primary explosive.[199] Due to the higher energy content of the C-N linkage (see chapter 6), as opposed to the C-C linkage, 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**) could therefore be a potentially interesting material for environmentally friendly primary explosives. Interestingly, despite the facile preparation which utilizes cheap and commercially available starting materials, it took almost 15 years until its properties for energetic material applications were investigated, mostly dealing with the use in a gas generator.[141,142] No data regarding its potential use as an explosive (primary and secondary) could be found.

The aim of this study has thus been the preparation and evaluation of some selected new salts of **79** for the application as energetic materials. These include metal salts (alkali and transition metals) as potential primary explosives and nitrogen-rich salts with hydroxylamine and triaminoguanidine, two of the most potent cations for high performance ionic secondary explosives.[137,200–203]

9.2 Results and Discussion

9.2.1 Syntheses

Scheme 9.1 illustrates the synthesis of 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**) by cyclization of 5-aminotetrazole with triethyl orthoformate and sodium azide in hot acetic acid, according



Scheme 9.1: Synthesis of 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**) from commercially available 5-amino-1*H*-tetrazole, and its salts **80**–**85**.

to the modified literature procedure.[140,204] The residue after removal of the volatile components (acetic acid, triethyl orthoformate) was dissolved in diluted hydrochloric acid and extracted with ethyl acetate, instead of direct extraction of the residue. This way **79** could be obtained analytically pure and free of unreacted 5-aminotetrazole. Following of the literature work-up method always yielded impure **79**.

The potassium (**82**), cesium (**83**), hydroxylammonium (**84**) and triaminoguanidinium (**85**) salts were prepared according to scheme 9.1 by simple acid-base reaction in ethanol or water using **79** and the corresponding carbonates or free bases. The silver salt **80** was prepared by the reaction of the neutral compound with silver nitrate in water. The copper(I) salt **81** was prepared according to the preparation of DBX-1 by the reaction of the in situ prepared sodium salt of **79** with copper(II) chloride in water and the subsequent reduction of copper(II) to copper(I) using sodium ascorbate.[28]

9.2.2 Crystal Structure Analysis

Hydroxylammonium 5-(tetrazol-1-yl)tetrazolate (**84**) crystallized in the orthorhombic space group *Pbca* with eight formula units in the unit cell. The calculated density at 173 K is only 1.561 g cm^{-3}, which is comparable to the ammonium salt (1.567 g cm^{-3} at 200 K).[204] The asymmetric unit, depicted in figure 9.1 together with the coordination sphere of the cation, consists of one ion pair. The structure of the anion is in agreement with that of the ammonium salt but displays an even larger N1–C1–N5–C2 torsion angle of $-151.6(1)°$ (ammonium salt: $-165.4(2)°$ for N4–C1–N5–C2), further lowering the conjugation between the two tetrazole rings. All protons of the hydroxylammonium cation are involved in a total of four strong hydrogen bonds, as depicted in figure 9.1 with the data in table 9.1.

Triaminoguanidinium 5-(tetrazol-1-yl)tetrazolate (**85**) crystallized in the orthorhombic space group $P2_12_12_1$ with four formula units in the unit cell. The calculated density at 173 K is 1.569 g cm^{-3}, which is interestingly higher than that of the hydroxylammonium

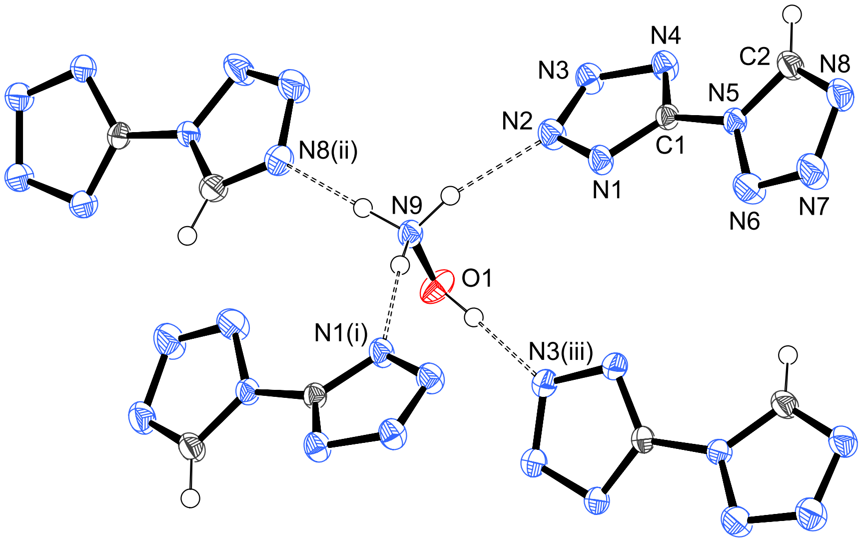


Figure 9.1: Coordination sphere of the cation in the crystal structure of hydroxylammonium 5-(tetrazol-1-yl)tetrazolate (**84**). Thermal ellipsoids at 50 % probability. Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+0.5, z-0.5$; (iii) $-x+0.5, y+0.5, z$.

Table 9.1: Hydrogen bonds present in hydroxylammonium 5-(tetrazol-1-yl)tetrazolate (**84**).

D–H···A	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	∠(D–H···A) / °
N9–H9A···N2	0.92(1)	1.97(1)	2.879(2)	167(1)
N9–H9B···N1$^{\mathrm{i}}$	0.93(3)	1.95(2)	2.857(1)	166(2)
N9–H9C···N8$^{\mathrm{ii}}$	0.96(2)	1.97(2)	2.903(1)	165(1)
O1–H1···N3$^{\mathrm{iii}}$	0.90(2)	1.82(2)	2.722(1)	177(2)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+0.5, z-0.5$; (iii) $-x+0.5, y+0.5, z$.

salt **84**. The asymmetric unit consists of one ion pair. The structure of the anion is also in agreement with that of the ammonium salt but displays a smaller N1–C1–N5–C2 torsion angle of 168.5(2)°. Although the structure is dominated by the hydrogen bonds emanating from the triaminoguanidinium cation, most of the interactions are fairly weak (D···A distance up to 0.2 Å above the sum of the van der Waals radii) and undirected (D–H···A angles mostly around 130°). The structure features a non-classical weak but quite directed C–H···N hydrogen bond, slightly below the sum of the van der Waals radii ($\sum r_{\mathrm{w}}(\mathrm{C,N}) = 3.25$ Å),[104] resulting in helical structures of anions along the *a* axis.

9.2.3 NMR Spectroscopy

In the ^{1}H NMR spectra, the C–H proton resonance is observed as a sharp signal at 10.21 ppm for neutral **79** and around 9.92 ppm in the salts **82**–**85**. The highly acidic N–H proton in **79** is found at 14.29 ppm also as a sharp signal. The proton resonance of the hydroxylammonium cation of **84** is at 10.20 ppm. The triaminoguanidinium cation of **85**

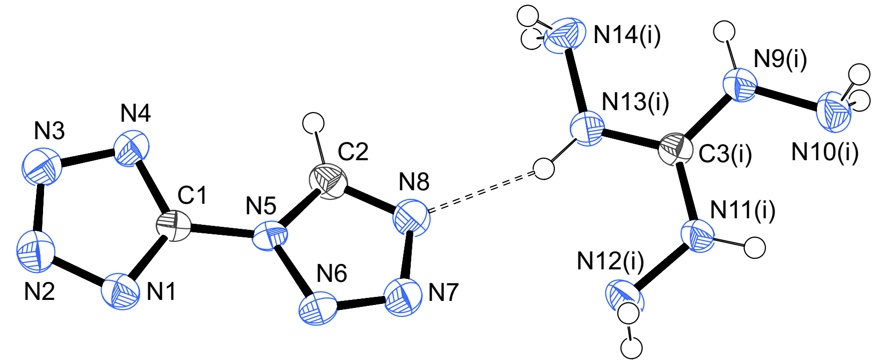


Figure 9.2: Molecular structure of triaminoguanidinium 5-(tetrazol-1-yl)tetrazolate (**85**). Thermal ellipsoids at 50 % probability. Symmetry code: (i) $x - 1, y, z$.

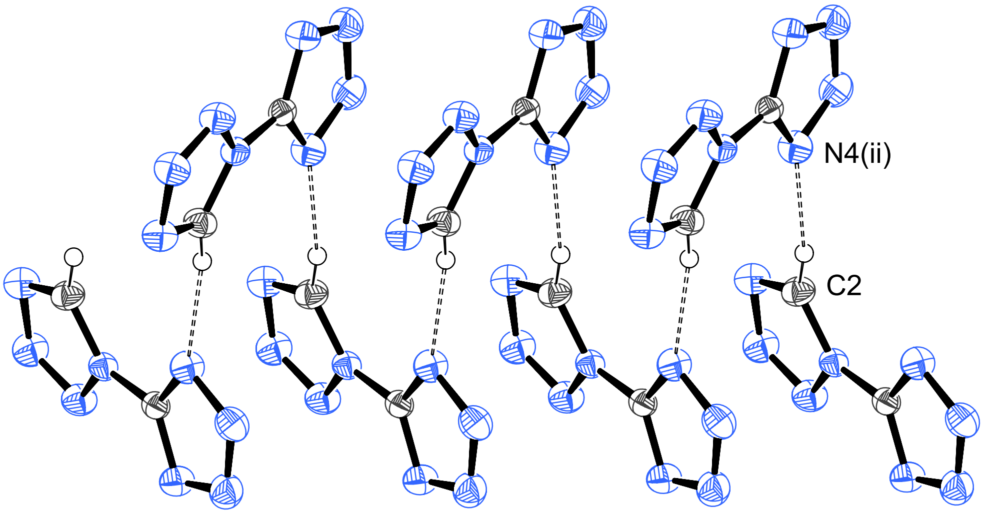


Figure 9.3: C–H$\cdots$N hydrogen bonding in triaminoguanidinium 5-(tetrazol-1-yl)tetrazolate (**85**). Thermal ellipsoids at 50 % probability. Symmetry code: (ii) $x - 0.5, -y + 0.5, -z$.

shows its usual signals at 9.92 (CH), 8.62 (NH) and 4.51 ppm (NH_2).

Both tetrazole carbon atoms can be observed in the ^{13}C NMR spectra, with C1 between 155.0 and 156.6 ppm and C2 between 143.3 and 144.2 ppm. In contrast to 1*H*-tetrazoles in which a deprotonation usually results in down field shifted carbon resonances (e.g. 5-amino-1*H*-tetrazole with 156.6 ppm and 5-aminotetrazolate with 164.8 ppm), here this effect is only marginal. The triaminoguanidinium cation of **85** exhibits a resonance at 159.1 ppm.

9.2.4 Thermal Stabilities

DSC measurements were performed in order to determine the thermal behavior of the synthesized compounds. The decomposition temperatures range from 128 °C (**81**) up to 197 °C (**82**). The nitrogen-rich salts **84** and **85**, as well as the cesium salt **83** show distinct melting points (130, 141 and 173 °C, respectively), although all melt under decomposition.

Table 9.2: Hydrogen bonds present in triaminoguanidinium 5-(tetrazol-1-yl)tetrazolate (**85**).

D–H···A	*d*(D–H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠(D–H···A) / °
$N14–H13\cdots N8^{iii}$	0.90(2)	2.13(2)	2.988(2)	159(2)
$N14–H14A\cdots N3^{ii}$	0.90(2)	2.26(2)	3.139(3)	163(2)
$C2–H2\cdots N4^{ii}$	0.99(2)	2.25(2)	3.215(3)	165(2)

Symmetry codes: (ii) $x - 0.5, -y + 0.5, -z$; (iii) $x + 1, y, z$.

While both the potassium (**82**) and the cesium (**83**) salt can be dehydrated, as evidenced per IR spectroscopy (missing O−H stretching vibration) and DSC (endothermic signal gone), both tend to rehydrate over time. The most thermally stable anhydrous metal salt is the silver salt **80** (186 °C), almost 60 °C more than the copper(I) salt **81**. This is interesting, because the copper(I) salt DBX-1 displays a decomposition around 300 °C, while silver 5-nitrotetrazolate decomposes between 210 and 250 °C.[205]

9.2.5 Sensitivities

The parent compound **79** has to be classified as extremely sensitive to impact (1 J), according to the UN recommendations, and can already be ignited by a slight hit with a small hammer. It is also extremely sensitive to friction (5 N) and should therefore only be handled with care. The same holds true for **80** and **81** (both < 1 J and < 5 N). The impact sensitivities of **79** $\cdot$ H_2O (1.5 J), **84** (3 J) and **85** (15 J) are significantly lower. However, **79** $\cdot$ H_2O and **84** are thus also classified as very sensitive and should therefore be handled with great care. Compound **85** is classified as sensitive, but is less sensitive than commonly used secondary explosives like RDX (7.4 J) and HMX (7 J). The same trends are observed regarding the friction sensitivities. While **79** $\cdot$ H_2O is still extremely sensitive to friction (8 N), **85** (160 N) exhibits a significantly lower sensitivity. Compound **84** again has to be classified as very sensitive (40 N). While the sensitivity to electrostatic discharge of **79** (130 mJ), **84** (150 mJ) and **85** (250 mJ) are in agreement to those observed for commonly used secondary explosives like RDX (200 mJ), compounds **81** (5 mJ) and **80** (10 mJ) are in the range of primary explosives like lead azide (5 mJ). Furthermore, compounds **79**, **80** and **81** are the only ones to always detonate (impact, friction and electrostatic discharge).

9.2.6 Energetic Properties

The silver (**80**) and copper(I) (**81**) salts were tested for their capability of being primary explosives by applying some basic heating tests. A small amount (approx. 5 mg) of **80** or **81**, respectively, was therefore heated on a spatula by a lighter, without direct flame contact. Both compounds detonated violently upon reaching their respective ignition temperatures.

Table 9.3: Energetic properties and detonation parameters of 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**), its two nitrogen-rich salts (**84**, **85**) and RDX.

	79	**84**	**85**	RDX
Formula	$C_2H_2N_8$	$C_2H_5N_9O$	$C_3H_{10}N_{14}$	$C_3H_6N_6O_6$
M / g mol^{-1}	138.09	171.12	242.2	222.12
IS / J	< 1	3	15	7.4
FS / N	< 5	40	160	120
ESD / mJ	130	150	250	200
N / %	81.14	73.67	80.96	37.84
$-\Omega$ / %	57.9	51.4	72.7	21.6
T_d / °C	145	136	145	204
ρ / g cm^{-3} [a]	1.728	1.561	1.569	1.824
$\Delta_f H°_{(s)}$ / kJ mol^{-1} [b]	622	628	859	85
$\Delta_f U°_{(s)}$ / kJ kg^{-1} [c]	4595	3776	3669	481
Calculated detonation parameters (EXPLO5 5.05)				
$-Q_v$ / kJ kg^{-1}	4769	5399	4223	6167
T_{ex} / K	3627	3769	2889	4242
p_{CJ} / kbar	282	257	241	361
D / m s^{-1}	8355	8227	8120	8844
V_0 / L mol^{-1}	706	789	806	738

[a] X-ray density; [b] calculated solid state enthalpy of formation; [c] calculated solid state energy of formation.

Next, a small sample (again approx. 5 mg) of either **80** or **81** was fixed onto a surface with a bit of transparent tape and poked by a preheated needle. Both compounds detonated instantly. Although both the potassium (**82**) and the cesium (**83**) salt were able to detonate when dried in an oven beforehand, both tended to rehydrate over time, as already mentioned (**82** to the dihydrate and **83** to the monohydrate). The initiation capability of the salts was therefore not tested.

The enthalpies of formation of **79**, **84**, **85** and RDX were calculated at the CBS-4M level of theory for better comparison, using the atomization energy method and utilizing experimental data. The results are summarized in table 9.3. All compounds exhibit highly endothermic enthalpies of formation between 562 and 859 kJ mol^{-1}, by far surpassing RDX (85 kJ mol^{-1}).

To estimate the detonation performances of the prepared compounds, selected key parameters were calculated using EXPLO5 (version 5.05),[206] and compared to RDX. The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker–Kistiakowsky–Wilson equation of state (BKW EOS) for gaseous detonation products and the Cowan–Fickett equation of state for solid carbon. The calculation of the equilibrium composition of the detonation products is done by applying the modified free energy minimization technique of White, Johnson and Dantzig. The program is designed to enable the calculation of detonation parameters at the Chapman–Jouguet point. The calculated detonation parameters using the experimentally determined densities and previously discussed enthalpies of formation are summarized in table 9.3. The utilized low-temperature crystal densities are of course slightly higher than those at room temperature, therefore the parameters are only of a comparative quality for a general estimation of the performances. Only the parent compound **79** exhibits decent performance characteristics with a calculated detonation velocity of 8355 $\mathrm{m\,s^{-1}}$ and a detonation pressure of 282 kbar, but still by far inferior to RDX (8844 $\mathrm{m\,s^{-1}}$, 361 kbar). This is the result of **79** possessing the highest density (1.728 $\mathrm{g\,cm^{-3}}$) of the neutral and nitrogen-rich ionic compounds. Although **84** incorporates the hydroxylammonium cation, often ensuring a high density and therefore in most cases the best performance concerning nitrogen-rich cations,[137] in this case it suffers from a low density (1.561 $\mathrm{g\,cm^{-3}}$), resulting in a poor performance (8227 $\mathrm{m\,s^{-1}}$, 257 kbar). The same holds true for the triaminoguanidinium salt **85**.

9.3 Conclusions

The goal of this project has been the optimization of the synthesis of 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**) and the preparation of several new metal and nitrogen-rich salts with silver (**80**), copper(I) (**81**), hydroxylammonium (**84**) and triaminoguanidinium (**85**). The structures of the two nitrogen-rich salts **84** and **85** were determined by low temperature single crystal X-ray crystallography. The decomposition temperatures, as evidenced by DSC, range from 128 °C (**81**) up to 197 °C (**82**). The sensitivities range from extremely sensitive (**79**, **80**, **81**: IS 1 J, FS 5 N) to sensitive (**85**: IS 15 J, FS 160 N), with **84** also showing rather high sensitivities (IS 3 J, FS 40 N). Although the initial behavior of the two primary explosives with silver (**80**) and copper(I) (**81**) seems promising, both suffer drawbacks. While the copper(I) cation of **81** is rather less toxic, a very low decomposition temperature of only 128 °C diminishes its potential application. Although **80** shows a reasonable thermal stability (186 °C), it is of academic interest only, due to the toxicity and high costs of silver. The much less toxic potassium (**82**) and cesium (**83**) salts also show tendencies as primary explosives, but only as long as they are in anhydrous form. Unfortunately, for primary explosive application, both rehydrate over time. The enthalpies of formation of **79**, **84** and **85** were predicted at the CSB-4M level of theory. All compounds are highly endothermic, especially **85** (859 $\mathrm{kJ\,mol^{-1}}$). Unfortunately, all compounds suffer from low densities, resulting in calculated detonation velocities between 7593 and 8355 $\mathrm{m\,s^{-1}}$, and detonation pressures between 213 and 282 kbar.

9.4 Experimental Part

5-(Tetrazol-1-yl)-2*H*-tetrazole (79)

Glacial acetic acid (50 mL) was added drop wise to a mixture of 5-aminotetrazole (8.50 g, 100 mmol), sodium azide (7.80 g, 120 mmol) and triethyl orthoformate (22.2 g, 150 mmol) at 60 °C under vigorous stirring. After stirring for four hours at 90 °C the obtained clear solution was cooled to room temperature and stirred with hydrochloric acid (2 M, 60 mL) for one hour. The solvent was completely evaporated under reduced pressure and the residue was suspended in toluene, then the solvent was evaporated again to remove traces of acetic acid. This procedure was repeated one more time, then the dry residue was dissolved in hydrochloric acid (0.5 M, 200 mL), extracted with ethyl acetate (4 × 50 mL) and the combined organic phases were dried over magnesium sulfate. After evaporation of the solvent under reduced pressure the residue was washed well with diethyl ether to yield anhydrous **79** as a colorless powder (5.80 g, 42.0 mmol, 42 %). Recrystallization from water furnishes the somewhat less sensitive monohydrate. ^{1}H NMR (DMSO-d_6): $\delta = 14.29$ (s, NH), 10.21 (s, CH). ^{13}C NMR (DMSO-d_6): $\delta = 155.0$ (C1), 143.8 (C2). IR (ATR): $\tilde{\nu} =$ 3163 (m), 3130 (m), 3034 (m), 2971 (m), 2865 (m), 2766 (m), 2702 (m), 2649 (m), 1697 (w), 1582 (vs), 1455 (m), 1385 (m), 1372 (m), 1272 (s), 1208 (m), 1178 (m), 1148 (m), 1114 (m), 1086 (s), 1021 (s), 993 (m), 957 (m), 913 (m), 891 (m), 871 (m), 742 (m), 649 (m) cm^{-1}. Raman (300 mW): $\tilde{\nu} = 3117$ (9), 1582 (100), 1543 (7), 1466 (6), 1275 (17), 1182 (10), 1162 (19), 1124 (14), 1094 (5), 1025 (32), 426 (14), 378 (13) cm^{-1}. MS (FAB−): $m/z =$ 137.1 ([M−H]$^-$). EA ($C_2H_2N_8$): calculated C 17.40, H 1.46, N 81.14 %; found C 18.02, H 1.55, N 79.29 %. DSC (5 °C min^{-1}): $T_\mathrm{d} = 134$ °C. Sensitivities (grain size < 100 µm): IS 1 J, FS 5 N, ESD 130 mJ.

Silver 5-(tetrazol-1-yl)tetrazolate (80)

Silver nitrate (357 mg, 2.10 mmol) in water (20 mL) was added drop wise to **79** (276 mg, 2.00 mmol) in water (20 mL) at 60 °C and the resulting suspension was stirred in the dark for 30 minutes. After cooling down the precipitate was filtered off and washed with water and ethanol to yield a colorless powder (431 mg, 1.76 mmol, 88 %). IR (ATR): $\tilde{\nu} = 3110$ (w), 1617 (w), 1586 (m), 1567 (vs), 1467 (m), 1453 (w), 1335 (w), 1264 (m), 1210 (w), 1184 (m), 1163 (w), 1141 (w), 1119 (w), 1092 (vs), 1026 (w), 996 (s), 958 (w), 887 (w), 738 (w), 716 (w), 708 (w) cm^{-1}. EA (C_2HAgN_8): calculated C 9.81, H 0.41, N 45.75 %; found C 10.30, H 0.63, N 45.03 %. DSC (5 °C min^{-1}): $T_\mathrm{d} = 186$ °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 10 mJ.

Copper(I) 5-(tetrazol-1-yl)tetrazolate (81)

A solution of **79** (276 mg, 2.00 mmol) in water (3 mL) and aqueous sodium hydroxide solution (2 M, 1 mL) was added to copper(II) chloride dihydrate (341 mg, 2.00 mmol) in water (14 mL) at 80 °C. The resulting blue suspension was heated to 90 °C and sodium ascorbate (198 mg, 1.00 mmol) in water (1 mL) was added drop wise. The suspension was refluxed for 15 minutes, cooled to room temperature and filtered. The residue was washed with water and ethanol then dried at 60 °C to yield a greyish powder (285 mg, 1.42 mmol, 71 %). IR (ATR): $\tilde{\nu}$ = 3128 (w), 1624 (w), 1558 (vs), 1474 (w), 1434 (w), 1346 (w), 1277 (w), 1175 (w), 1083 (s), 1029 (w), 997 (s), 956 (w), 871 (w), 734 (w), 709 (w), 657 (m) $\mathrm{cm^{-1}}$. EA (C_2HCuN_8): calculated C 11.97, H 0.50, N 55.85 %; found C 11.88, H 1.02, N 50.76 %. DSC ($5\,^\circ\mathrm{C\,min^{-1}}$): $T_\mathrm{d} = 128\,^\circ\mathrm{C}$. Sensitivities (grain size $< 100\,\mu\mathrm{m}$): IS < 1 J, FS < 5 N, ESD 5 mJ.

Potassium 5-(tetrazol-1-yl)tetrazolate (82)

Potassium carbonate (138 mg, 1.00 mmol) and **79** (276 mg, 2.20 mmol) were refluxed in ethanol (60 mL) until a clear solution was obtained. It was filtered, the solvent was evaporated under reduced pressure and the residue was stirred in ethyl acetate, filtered off and washed with diethyl ether to yield a colorless powder (288 mg, 1.63 mmol, 82 %). ^{1}H NMR (DMSO-d_6): $\delta = 9.95$ (s, CH). ^{13}C NMR (DMSO-d_6): $\delta = 155.3$ (C1), 143.4 (C2). IR (ATR): $\tilde{\nu}$ = 3372 (m), 3146 (m), 1652 (w), 1566 (w), 1548 (vs), 1480 (m), 1464 (m), 1437 (w), 1336 (w), 1260 (m), 1204 (w), 1180 (m), 1138 (w), 1096 (vs), 1035 (w), 995 (s), 963 (m), 874 (m), 796 (w), 736 (m), 692 (w), 656 (w) $\mathrm{cm^{-1}}$. MS (FAB+): $m/z = 39.0$ ([K]$^+$). (FAB−): $m/z = 137.2$ ($[C_2HN_8]^-$). EA (C_2HKN_8): calculated C 13.63, H 0.57, N 63.60 %; found C 13.92, H 1.18, N 61.52 %. DSC ($5\,^\circ\mathrm{C\,min^{-1}}$): $T_\mathrm{d} = 197\,^\circ\mathrm{C}$.

Cesium 5-(tetrazol-1-yl)tetrazolate (83)

Cesium carbonate (326 mg, 1.00 mmol) and **79** (276 mg, 2.20 mmol) were refluxed in ethanol (60 mL) until a clear solution was obtained. It was filtered, the solvent was evaporated under reduced pressure and the residue was stirred in ethyl acetate, filtered off and washed with diethyl ether to yield a colorless powder (491 mg, 1.82 mmol, 91 %). ^{1}H NMR (DMSO-d_6): $\delta = 9.92$ (s, 1H, CH). ^{13}C NMR (DMSO-d_6): $\delta = 155.2$ (C1), 143.3 (C2). IR (ATR): $\tilde{\nu}$ = 3047 (m), 1561 (w), 1538 (s), 1478 (s), 1464 (m), 1426 (m), 1337 (w), 1324 (w), 1250 (s), 1196 (m), 1185 (m), 1141 (w), 1124 (w), 1095 (vs), 1071 (m), 1028 (w), 1012 (w), 990 (vs), 963 (m), 941 (m), 834 (w), 737 (m), 712 (w), 664 (m) $\mathrm{cm^{-1}}$. MS (FAB+): $m/z = 133.0$ ([Cs]$^+$). (FAB−): $m/z = 137.2$ ($[C_2HN_8]^-$). EA (C_2HCsN_8): calculated C 8.90, H 0.37, N 41.50 %; found C 8.79, H 0.60, N 39.46 %. DSC ($5\,^\circ\mathrm{C\,min^{-1}}$): $T_\mathrm{m} = 173\,^\circ\mathrm{C}$ (equals T_d).

Hydroxylammonium 5-(tetrazol-1-yl)tetrazolate (84)

Hydroxylamine hydrate (50 %, 661 mg, 10.0 mmol) was added to **79** (1.38 g, 10.0 mmol) in water (20 mL) and refluxed for 15 minutes. The solvent was evaporated under reduced pressure and the residue was washed with ethanol and diethyl ether to yield a colorless solid (1.40 g, 8.18 mmol, 82 %). ^{1}H NMR (DMSO-d_6): $\delta = 9.92$ (s, CH). ^{13}C NMR (DMSO-d_6): $\delta = 155.2$ (C1), 143.3 (C2). IR (ATR): $\tilde{\nu} = 3137$ (m), 2966 (m), 2829 (m), 2700 (s), 2129 (w), 1643 (w), 1580 (w), 1556 (s), 1522 (m), 1477 (s), 1458 (m), 1437 (m), 1345 (w), 1268 (s), 1241 (m), 1214 (m), 1179 (s), 1161 (m), 1148 (m), 1112 (w), 1091 (vs), 1039 (m), 995 (vs), 969 (s), 884 (m), 779 (m), 738 (m), 725 (m), 713 (m), 669 (w), 655 (s) cm^{-1}. MS (FAB+): $m/z = 34.0$ ([NH$_3$OH]$^+$). (FAB−): $m/z = 137.2$ ([C$_2$HN$_8$]$^-$). EA (C$_2$H$_5$N$_9$O): calculated C 14.04, H 2.95, N 73.67 %; found C 14.72, H 2.91, N 73.30 %. DSC (5 °C min^{-1}): $T_\mathrm{m} = 130$ °C (equals T_d). Sensitivities (grain size < 100 µm): IS 3 J, FS 40 N, ESD 150 mJ.

Triaminoguanidinium 5-(tetrazol-1-yl)tetrazolate (85)

Triaminoguanidine (991 mg, 9.52 mmol) was added to **79** (1.38 g, 10.0 mmol) in hot ethanol (30 mL). Water was added until a clear solution was obtained, then refluxed for 15 minutes. The solvent was evaporated under reduced pressure and the residue was washed with ethanol and diethyl ether to yield a colorless solid (1.40 g, 5.78 mmol, 61 %). ^{1}H NMR (DMSO-d_6): $\delta = 9.92$ (s, 1H, CH), 8.62 (s, 3H, NH), 4.51 (s, 6H, NH$_2$). ^{13}C NMR (DMSO-d_6): $\delta = 159.1$ (TAG$^+$), 155.2 (C1), 143.3 (C2). IR (ATR): $\tilde{\nu} = 3366$ (w), 3333 (m), 3194 (m), 3080 (m), 1689 (vs), 1606 (m), 1568 (w), 1546 (s), 1475 (m), 1461 (m), 1434 (w), 1352 (m), 1336 (w), 1259 (m), 1188 (w), 1133 (vs), 1096 (vs), 988 (vs), 962 (vs), 736 (m), 701 (w), 661 (w) cm^{-1}. Raman (300 mW): $\tilde{\nu} = 3321$ (8), 3235 (17), 1681 (12), 1547 (100), 1433 (19), 1321 (9), 1259 (21), 1196 (6), 1142 (36), 1095 (11), 1083 (19), 1032 (30), 885 (26), 737 (9), 639 (11) cm^{-1}. MS (FAB+): $m/z = 105.0$ ([CH$_9$N$_6$]$^+$). (FAB−): $m/z = 137.2$ ([C$_2$HN$_8$]$^-$). EA (C$_3$H$_{10}$N$_{14}$): calculated C 14.88, H 4.16, N 80.96 %; found C 15.11, H 3.77, N 76.67 %. DSC (5 °C min^{-1}): $T_\mathrm{m} = 141$ °C (equals T_d). Sensitivities (grain size < 100 µm): IS 15 J, FS 160 N, ESD 250 mJ.

Transition Metal Salts of Nitramines

unpublished results

10.1 Introduction

Nitraminoazoles exhibit lower enthalpies of formation than azidoazoles, but typically show higher thermal stabilities and especially higher densities. One possible candidate for investigation is 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) (**86**),[131] due to the previous studies on 5,5′-diazido-3,3′-bis(1*H*-1,2,4-triazole) (**53**, see chapter 7) and their common precursor 5,5′-diamino-3,3′-bis(1*H*-1,2,4-triazole) (**52**). Another interesting 1,2,4-triazole-based nitramine displaying a good thermal stability (242 °C), rather high sensitivities (IS 1 J, FS 60 N) and apparently no reported metal salts is bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane.[207] Both compounds can be prepared in facile syntheses and were thus preferred over nitramine analogues of several of the investigated azides, like 5-(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole,[208] or 5-(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole.[139] 3-Azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**) has already been investigated in a previous chapter, while, for example, 5-nitramino-3-nitro-1*H*-1,2,4-triazole had not been investigated due to its very low reported thermal stability of 135 °C.[107] Concerning tetrazoles, although practically all 5-substituted tetrazole derivatives had already been investigated as potential primary explosive forming compounds, only few reports concerning metal salts (mostly alkali and alkaline earth) of the rather simple 5-nitrimino-1,4*H*-tetrazole could be found.[204,209–214] The calcium[212] and silver[214] salts of the divalent anion are both primary explosives with high thermal stabilities (well above 200 °C). Furthermore, the cadmium salt is reported with an excellent thermal stability (333 °C).[204]

The previous chapters mainly only dealt with silver, copper and alkali metal cations to investigate the applicability of the anions as primary explosives, although there are other potentially suitable transition and main group metal cations, as has been mentioned in the introductory chapter. Thus it was of interest to prepare additional metal salts with a wide range of less toxic transition metals like manganese, iron, cobalt, nickel, copper, zinc and investigate their energetic performances and also hydration levels, because the latter tends to be a problem due to the known high affinity of those cations towards water. Other possible cations are chromium, cadmium, mercury, thallium and lead, which are quite toxic but were used in primary explosive formulations in the past,[2,4,12] and can thus be of comparative value concerning the thermal stability and energetic performance.

10.2 Results and Discussion

10.2.1 Syntheses

5,5′-Dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) dihydrate (**86**) was prepared according to a published procedure by the nitration of 5,5′-diamino-3,3′-bis(1*H*-1,2,4-triazole) (**52**) with nitric acid in sulfuric acid.[215] Bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane and 5-nitrimino-1,4*H*-tetrazole were taken from the laboratory inventory.

The metal salts were prepared by the addition of the corresponding metal chlorides, nitrates or acetates to the in situ prepared sodium salt of the neutral compound in water at elevated temperatures and subsequent precipitation of the salt.

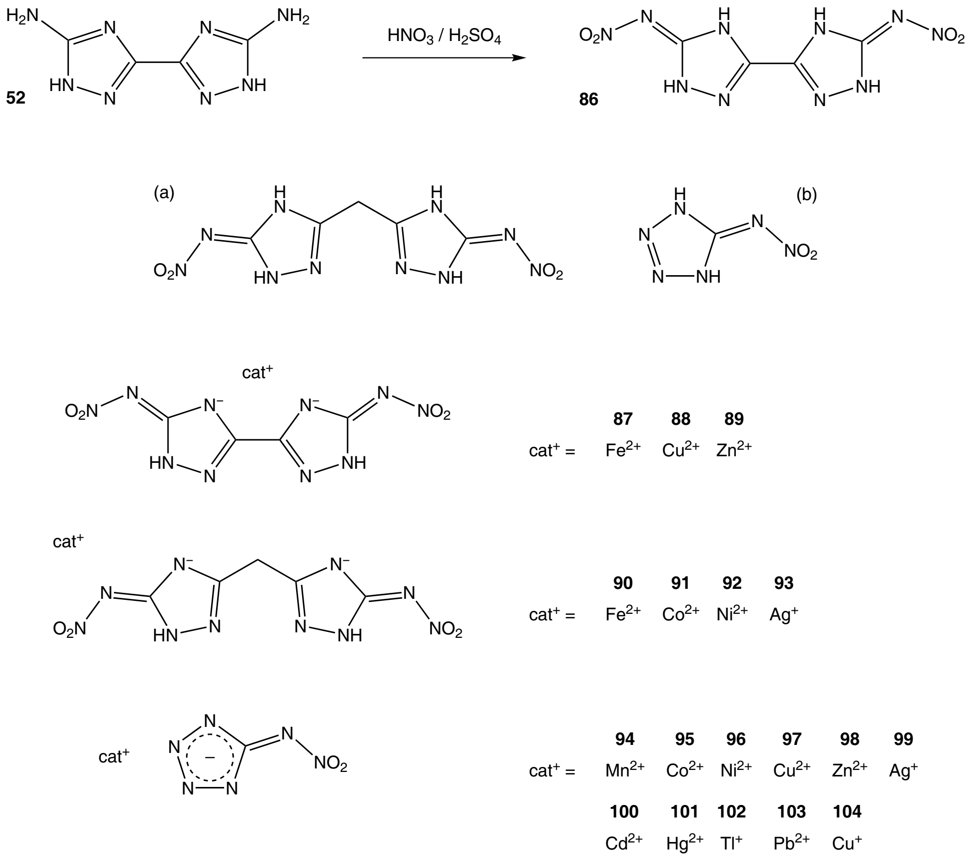
Unfortunately, as expected, almost all of the obtained metal salts are polyhydrates and only three salts of 5-nitrimino-1,4*H*-tetrazole (**99**, **102**, **103**) are anhydrous. Interestingly, the attempted syntheses of the cobalt(II) and nickel salts of 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) (**86**) resulted in highly gelatinous thick solutions. The syntheses of the iron(II), iron(III) and chromium(III) salts of 5-nitrimino-1,4*H*-tetrazole were also not successful.

10.2.2 Crystal Structure Analysis

While nickel bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane usually precipitated in the form of a tetrahydrate (**92**), single crystals of a hexahydrate ($\mathbf{92} \cdot 2\,\mathrm{H_2O}$) could be obtained from a strongly diluted solution. It crystallized in the orthorhombic space group *Pnma* with four molecular units in the unit cell. The main molecular unit consists of a nickel central atom, one doubly deprotonated 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) and four water molecules as ligands, forming a nearly regular octahedron (Ni1–N1: 2.102(2) Å; Ni1–O3: 2.034(2) Å; Ni1–O4: 2.106(2) Å; Ni1–O5: 2.073(2) Å; N1–Ni1–O3: 94.11(5)°; N1–Ni1–O4: 88.08(5)°; N1–Ni1–N1$^{\mathrm{i}}$: 88.83(7)°; N1–Ni1–O5$^{\mathrm{i}}$: 92.14(7)°). The structure contains two additional and disordered (54:46) water molecules and is illustrated in figure 10.1. One of the water molecules of the complex unit (O4) shows two different orientations of the protons, which is also resulting in a disorder (50:50). The hydrogen bonds emanating from the water molecules and the ligand lead to the formation of antiparallel linear chains along the *a* axis, illustrated in figure 10.2.

10.2.3 Thermal Stabilities, Sensitivities and Energetic Properties

Due to the low solubility of the compounds and their ionic nature only elemental analysis proved to be suitable for identification. While the metal salts **87**–**89** and **90**–**93** of 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) (**86**) and bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane, respectively, have a fixed amount of hydration (mostly around four, but up to



Scheme 10.1: Overview of the investigated compounds 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) (**86**), bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane (a), 5-nitrimino-1,4*H*-tetrazole (b) and their corresponding metal salts **87**–**104**.

seven water molecules) and show a very good agreement between calculated and found values, the hydrated metal salts **94**–**104** of 5-nitrimino-1,4*H*-tetrazole have all mixed amounts of hydration, thus preventing the formulation of clear sum formulas. This is quite similar to the metal salts of 1,2-bis(1*H*-tetrazol-5-yl)diazene and 1,3-bis(1*H*-tetrazol-5-yl)triazene.[32,33]

The thermal stability of **87**–**93** was analyzed by DTA and **94**–**104** by DSC. Interestingly, for both 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) (**86**) and bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane the iron(II) salt (**87**, **90**) is the least temperature stable with an onset of decomposition in the vicinity of 150 °C. The other metal salts are more thermally stable, but all decompose below 200 °C. The most stable is the nickel salt **92** (198 °C). Nitrogen-rich salts of **86** are mostly well above 200 °C,[131] while its barium salt decomposes above 330 °C and the lead salt at 209 °C.[216] Concerning bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane, only the guanidinium and triaminoguanidinium salts could be found in the literature and both are reported to decompose slightly above 205 °C.[207] Salts **94**–**104** decompose in the range of 184 to 326 °C, while only the mercury salt **101** is below 200 °C. The highest thermal stability is exhibited by the already known cadmium salt.

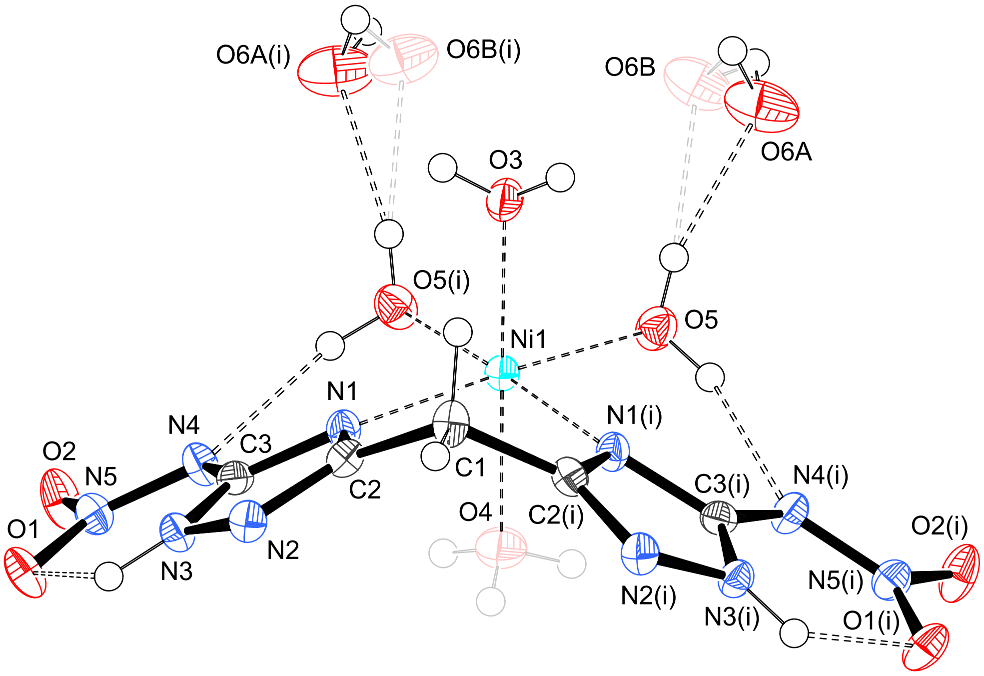


Figure 10.1: Molecular structure of nickel bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane hexahydrate (**92** $\cdot$ 2 H_2O). Thermal ellipsoids at 50 % probability. Disordered atoms / molecule groups are shown faded. Symmetry code: (i) $x, -y+0.5, z$.

Concerning the sensitivities to impact and friction of the triazole based metal salts **87**–**89** and **90**–**92**, all six compounds are completely insensitive, probably due to the high degree of hydration. Only the silver salt **93** shows rather high sensitivities (3 J, 96 N), but it is also the one with the lowest water content (monohydrate). The metal salts of 5-nitrimino-1,4*H*-tetrazole are comparatively more sensitive, with mostly 10 J impact sensitivity, also due to hydration. None of them shows an impact-to-detonation or friction-to-detonation transition. The sensitivities of the investigated compounds are compiled in table 10.1.

All compounds were subjected to slow heating on a metal spatula in the usual fashion to investigate the general capability for a DDT. None of the triazole based metal salts **87**–**93** show any sign of a DDT, only slight sparkling. The metal salts **94**–**104** of 5-nitrimino-1,4*H*-tetrazole on the other hand all detonated violently, except for the thallium salt **102** which decomposed into a red cloud. Unfortunately, due to the hydration, none of the compounds, except for the water free silver (**99**) and lead (**103**) salts, were capable of a DDT upon rapid heating (hot-needle test). It was also not possible to completely dehydrate any of the compounds. At the very least one water molecule always remained, as evidenced by elemental analysis and infrared spectroscopy.

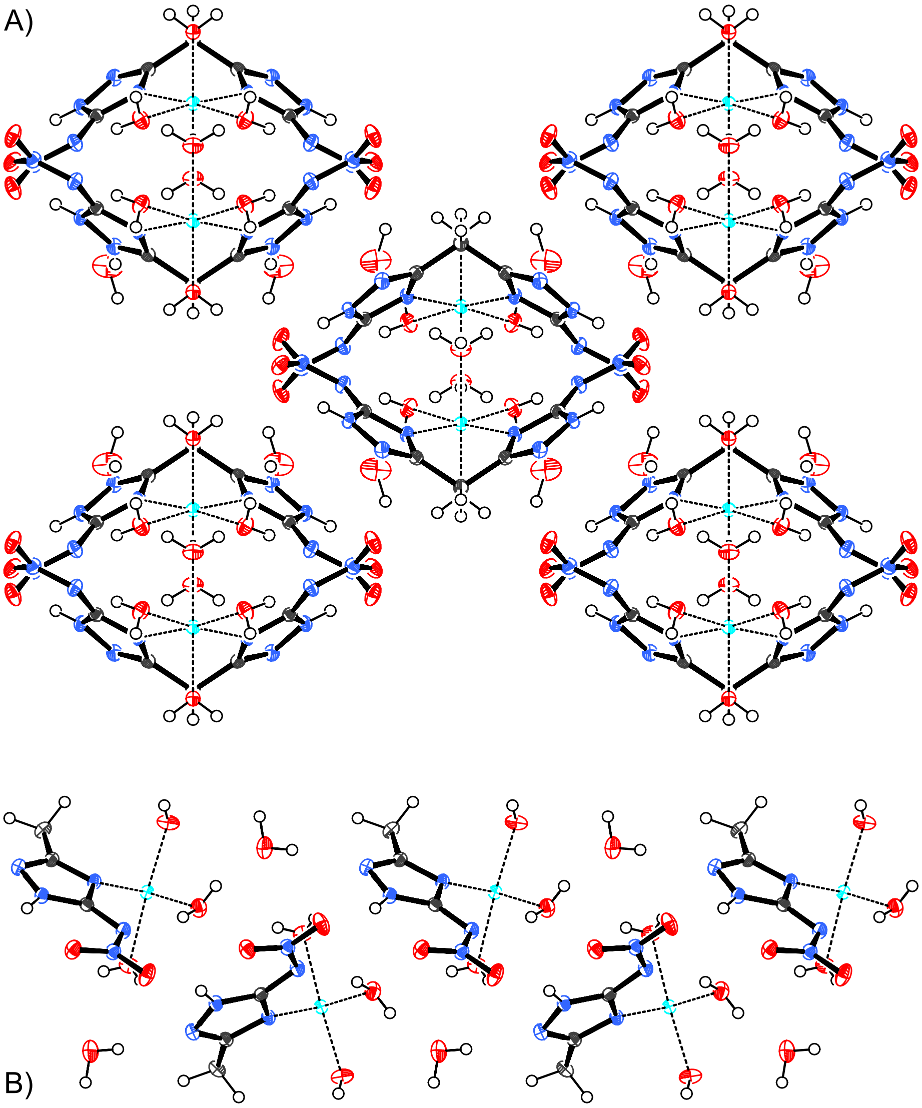


Figure 10.2: Chains of molecular units in nickel bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane hexahydrate (**92** $\cdot\, 2\,H_2O$). A) View along the *a* axis; B) side view on a chain. Thermal ellipsoids at 50 % probability. Disordered water molecules left out for clarity.

10.3 Conclusions

The goal of this investigation has been the potential suitability of transition metal salts of 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) (**86**), bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane and 5-nitrimino-1,4*H*-tetrazole as environmentally friendly primary explosives with higher thermal stability than the various azidotriazoles of the previous chapters. Unfortunately, practically all of the obtained compounds are hydrates and it was in no case possible to completely dehydrate them. The few exceptions contain either expensive or toxic cations (silver, thallium, lead), which served only as comparison regarding performance and thermal stability. None of the metal salts **87**–**93** of 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-

Table 10.1: Energetic properties of the investigated compounds **87**–**104**.

Compound	Cation	H_2O [a]	IS / J	FS / N	T_d / °C	DDT	fast heating
87	Fe(II)	yes	— [b]	— [b]	154	no	—
88	Cu(II)	yes	— [b]	— [b]	165	no	—
89	Zn	yes	— [b]	— [b]	186	no	—
90	Fe(II)	yes	40	360	140	no	—
91	Co(II)	yes	40	360	159	no	—
92	Ni	yes	40	360	198	no	—
93	Ag	yes	3	96	182	no	—
94	Mn	yes	10	120	283	yes	deflagration
95	Co(II)	yes	10	192	263	yes	deflagration
96	Ni	yes	10	192	302	yes	deflagration
104	Cu(I)	yes	10	30	219	yes	deflagration
97	Cu(II)	yes	10	96	233	yes	deflagration
98	Zn	yes	10	360	304	yes	deflagration
99	Ag	no	3[214]	56[214]	294	yes	detonation
100	Cd	yes	17[204]	12[204]	326	yes	deflagration
101	Hg	yes	— [c]	— [c]	184	yes	deflagration
102	Tl	no	— [c]	— [c]	302	no	deflagration
103	Pb	no	— [c]	— [c]	290	yes	detonation

[a] Is the compound a hydrate? [b] Not exactly determined, similar to **90**–**92**; [c] not determined due to toxicity concerns.

triazole) (**86**) and bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane were capable of a DDT. Although all except for one (the thallium salt **102**) of the salts **94**–**104** of 5-nitrimino-1,4*H*-tetrazole are capable of a DDT when heated slowly, only the water free silver (**99**) and lead (**103**) salts detonated when heated rapidly. The compounds are therefore most probably not suited for practical applications, despite high thermal stabilities (mostly well above 250 °C). The results are similar to the salts of bis(1*H*-tetrazol-5-yl)amine,[31] 1,2-bis(1*H*-tetrazol-5-yl)diazene,[32] and 1,3-bis(1*H*-tetrazol-5-yl)triazene,[33] which were nevertheless patented as ingredients in primary explosive formulations.

10.4 Experimental Part

5,5′-Dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) dihydrate (86)

Nitric acid (100 %, 12 mL) was added drop wise to **52** (4.00 g, 24.1 mmol) in sulfuric acid (98 %, 40 mL) at 0 °C, then stirred for one hour at room temperature. The solution was poured on ice (100 g), the precipitate was filtered off, washed with water and recrystallized from boiling water (about 750 mL) to yield a pale yellow solid (4.26 g, 14.6 mmol, 61 %).

^{1}H NMR (DMSO-d_6): δ = 14.57 (vbr), 5.02 (br). ^{13}C NMR (DMSO-d_6): δ = 153.0, 142.0. ^{14}N NMR (DMSO-d_6): $\delta = -14$ (NO_2). MS (FAB−): m/z = 255.3 ([M−H]$^-$). EA ($C_4H_4N_{10}O_4 \cdot 2\,H_2O$): calculated C 16.44, H 2.76, N 47.94 %; found C 16.70, H 2.73, N 47.75 %.

General method for salts 87–93

Iron(II) sulfate heptahydrate (1.00 mmol), cobalt(II) acetate tetrahydrate (1.00 mmol), nickel acetate tetrahydrate (1.00 mmol), copper(II) sulfate pentahydrate (1.00 mmol) or silver nitrate (1.00 mmol), respectively, in water (10 mL) was added to **86** (292 mg, 1.00 mmol) or bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane (270 mg, 1.00 mmol) in a mixture of water (40 mL) and sodium hydroxide solution (2 M, 1.0 mL, 2.0 mmol) at 60 °C. The reaction mixture was stirred for an additional ten minutes, then left for crystallization. The precipitate was filtered off and washed with water and ethanol. The silver salt **93** was dried at 70 °C for three days.

Iron(II) 5,5′-dinitrimino-3,3′-bis(1*H*-1,2,4-triazolate) tetrahydrate (87)

Pale brown solid (249 mg, 6.52 µmol, 65 %). IR (ATR): $\tilde{\nu}$ = 3218 (m), 1523 (s), 1448 (vs), 1277 (vs), 1090 (m), 986 (m), 861 (w), 732 (m) cm^{-1}. EA ($C_4H_2FeN_{10}O_4 \cdot 4\,H_2O$): calculated C 12.58, H 2.64, N 36.66 %; found C 12.73, H 2.58, N 35.64 %. DTA (5 °C min^{-1}): T_d = 154 °C.

Copper(II) 5,5′-dinitrimino-3,3′-bis(1*H*-1,2,4-triazolate) pentahydrate (88)

Pale green solid (281 mg, 6.89 µmol, 69 %). IR (ATR): $\tilde{\nu}$ = 3074 (m), 1663 (w), 1630 (w), 1560 (m), 1544 (m), 1516 (m), 1454 (s), 1407 (m), 1343 (s), 1298 (vs), 1261 (vs), 1113 (s), 1070 (m), 1020 (m), 870 (w), 851 (w), 811 (m), 777 (m), 736 (s) cm^{-1}. EA ($C_4H_2CuN_{10}O_4 \cdot 5\,H_2O$): calculated C 11.78, H 2.97, N 34.55 %; found C 12.36, H 2.91, N 34.88 %. DTA (5 °C min^{-1}): T_d = 165 °C.

Zinc 5,5′-dinitrimino-3,3′-bis(1*H*-1,2,4-triazolate) tetrahydrate (89)

Pale yellow solid (328 mg, 8.38 µmol), 84 %). IR (ATR): $\tilde{\nu}$ = 3108 (m), 1611 (w), 1544 (s), 1504 (m), 1444 (s), 1388 (w), 1341 (vs), 1286 (vs), 1236 (vs), 1100 (vs), 1055 (m), 1019 (s), 987 (w), 862 (w), 780 (m), 714 (vs) cm^{-1}. EA ($C_4H_2N_{10}O_4Zn \cdot 4\,H_2O$): calculated C 12.27, H 2.57, N 35.77 %; found C 12.59, H 2.57, N 35.47 %. DTA (5 °C min^{-1}): T_d = 186 °C.

Iron(II) bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane heptahydrate (90)

Brown-yellow solid (406 mg, 9.02 µmol, 90 %). IR (ATR): $\tilde{\nu}$ = 3206 (s), 2360 (w), 1636 (w), 1529 (s), 1514 (s), 1455 (m), 1343 (vs), 1262 (s), 1135 (m), 1100 (s), 1008 (m), 929 (w), 875 (w), 821 (w), 804 (w), 762 (w), 744 (w), 715 (s) cm^{-1}. EA ($C_5H_4FeN_{10}O_4 \cdot 4\,H_2O$): calculated C 13.34, H 4.03, N 31.12 %; found C 13.63, H 3.85, N 31.02 %. DTA (5 °C min^{-1}): T_d = 140 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 250 mJ.

Cobalt(II) bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane hexahydrate (91)

Small orange crystals (389 mg, 8.94 µmol, 89 %). IR (ATR): $\tilde{\nu}$ = 3216 (vs), 2360 (w), 2335 (w), 1646 (w), 1531 (s), 1518 (s), 1457 (m), 1342 (vs), 1264 (vs), 1134 (m), 1102 (vs), 1009 (m), 930 (w), 876 (w), 822 (w), 804 (w), 762 (w), 745 (w), 716 (m) cm^{-1}. EA ($C_5H_4CoN_{10}O_4 \cdot 6\,H_2O$): calculated C 13.80, H 3.71, N 32.19 %; found C 13.84, H 3.95, N 32.11 %. DTA (5 °C min^{-1}): T_d = 159 °C. Sensitivities (grain size 100 to 500 µm): IS 40 J, FS 360 N, ESD 200 mJ.

Nickel bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane tetrahydrate (92)

Blue-green powder (301 mg, 7.55 µmol, 76 %). IR (ATR): $\tilde{\nu}$ = 3564 (w), 3382 (w), 3165 (w), 3035 (w), 2362 (w), 1652 (w), 1562 (w), 1525 (s), 1457 (m), 1422 (m), 1401 (m), 1388 (m), 1314 (vs), 1280 (vs), 1225 (m), 1154 (m), 1098 (w), 1072 (m), 1052 (m), 1010 (m), 933 (w), 882 (w), 865 (w), 795 (w), 770 (w), 762 (w), 745 (w), 724 (w), 703 (m), 663 (m) cm^{-1}. EA ($C_5H_4N_{10}NiO_4 \cdot 4\,H_2O$): calculated C 15.05, H 3.03, N 35.11 %; found C 15.32, H 2.88, N 35.12 %. DTA (5 °C min^{-1}): T_d = 198 °C. Sensitivities (grain size < 100 µm): IS 40 J, FS 360 N, ESD 200 mJ.

Disilver bis(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)methane monohydrate (93)

Brown solid (460 mg, 9.17 µmol, 92 %). IR (ATR): $\tilde{\nu}$ = 3401 (w), 2360 (w), 2336 (w), 1623 (w), 1532 (s), 1420 (s), 1368 (w), 1263 (vs), 1134 (m), 1111 (s), 1045 (w), 1000 (m), 922 (w), 898 (w), 838 (w), 762 (w), 736 (w), 712 (w), 688 (w), 658 (w) cm^{-1}. EA ($C_5H_4AgN_{10}O_4 \cdot H_2O$): calculated C 11.97, H 1.20, N 27.91 %; found C 12.08, H 1.17, N 27.67 %. DSC (5 °C min^{-1}): T_d = 182 °C. Sensitivities (grain size 500 to 1000 µm): IS 3 J, FS 96 N, 100 mJ.

General method for salts 94–103

5-Nitrimino-1,4*H*-tetrazole (130 mg, 1.00 mmol) in a mixture of water (3 mL) and sodium hydroxide solution (2 M, 1.0 mL) was added drop wise to the metal salt (manganese nitrate tetrahydrate, cobalt(II) chloride hexahydrate, nickel chloride hexahydrate, copper(II) chloride dihydrate, zinc chloride, silver nitrate, cadmium chloride pentahemihydrate, mercury acetate, thallium nitrate, lead nitrate; 1.00 mmol) in water (14 mL) at 90 °C. The resulting suspension was refluxed for 15 minutes or up to one hour, then cooled down to room temperature under stirring. The precipitate was filtered off, washed with water, ethanol and diethyl ether, then dried in air.

Manganese 5-nitriminotetrazolate hydrate (94)

Pale brown Solid (148 mg). IR (ATR): $\tilde{\nu}$ = 3509 (w), 3192 (w), 1650 (w), 1496 (s), 1474 (vs), 1434 (vs), 1410 (vs), 1293 (vs), 1279 (vs), 1226 (w), 1182 (w), 1168 (m), 1140 (w), 1097 (w), 1040 (w), 1019 (vs), 871 (m), 766 (w), 752 (w), 736 (w), 666 (w) cm^{-1}. EA ($CMnN_6O_2$): calculated C 6.56, H 0.0, N 45.93 %; found C 5.63, H 1.80, N 35.38 %. DSC (5 $°\text{C min}^{-1}$): T_d = 283 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 120 N.

Cobalt(II) 5-nitriminotetrazolate hydrate (95)

Peach-colored solid (248 mg). IR (ATR): $\tilde{\nu}$ = 3323 (s), 3124 (m), 1640 (w), 1488 (vs), 1418 (vs), 1390 (vs), 1328 (vs), 1193 (m), 1160 (w), 1114 (m), 1050 (w), 1037 (m), 884 (m), 748 (m), 718 (w) cm^{-1}. EA ($CCoN_6O_2$): calculated C 6.42, H 0.0, N 44.95 %; found C 5.27, H 2.98, N 31.67 %. DSC (5 $°\text{C min}^{-1}$): T_d = 263 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 192 N.

Nickel 5-nitriminotetrazolate hydrate (96)

Pale blue solid (54 mg). IR (ATR): $\tilde{\nu}$ = 3377 (m), 1634 (w), 1488 (s), 1432 (s), 1381 (vs), 1298 (s), 1140 (w), 1064 (w), 1019 (m), 872 (w), 754 (w) cm^{-1}. EA (CN_6NiO_2): calculated C 6.43, H 0.0, N 45.00 %; found C 5.16, H 2.88, N 31.32 %. DSC (5 $°\text{C min}^{-1}$): T_d = 302 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 192 N.

Copper(II) 5-nitriminotetrazolate hydrate (97)

Blue-green solid (176 mg). IR (ATR): $\tilde{\nu}$ = 3484 (m), 1634 (w), 1488 (vs), 1425 (vs), 1387 (vs), 1294 (vs), 1267 (s), 1228 (w), 1211 (w), 1139 (m), 1059 (w), 1011 (s), 870 (m), 769 (w), 749 (m), 706 (w) cm^{-1}. EA ($CCuN_6O_2$): calculated C 6.27, H 0.0, N 43.86 %; found C 5.35, H 2.12, N 30.84 %. DSC (5 $°\text{C min}^{-1}$): T_d = 233 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 96 N.

Zinc 5-nitriminotetrazolate hydrate (98)

Colorless solid (192 mg). IR (ATR): $\tilde{\nu}$ = 3434 (m), 1641 (w), 1489 (vs), 1435 (s), 1386 (vs), 1341 (vs), 1187 (w), 1130 (w), 1115 (w), 1039 (m), 998 (w), 867 (w), 845 (w), 754 (m), 740 (w), 688 (w) cm^{-1}. EA (CN_6O_2Zn): calculated C 6.21, H 0.0, N 43.45 %; found C 5.52, H 2.49, N 31.21 %. DSC ($5\,°\text{C}\,\text{min}^{-1}$): T_d = 304 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 360 N.

Disilver 5-nitriminotetrazolate (99)

Colorless solid (338 mg, 9.86 µmol, 97 %). IR (ATR): $\tilde{\nu}$ = 3462 (w), 1611 (w), 1463 (s), 1428 (m), 1408 (m), 1362 (m), 1291 (vs), 1245 (s), 1188 (m), 1172 (m), 1146 (w), 1113 (m), 1040 (w), 1022 (m), 896 (w), 759 (w), 741 (w), 719 (w) cm^{-1}. EA ($CAg_2N_6O_2$): calculated C 3.49, H 0.0, N 24.45 %; found C 3.34, H 0.0, N 23.81 %. DSC ($5\,°\text{C}\,\text{min}^{-1}$): T_d = 294 °C.

Cadmium 5-nitriminotetrazolate hydrate (100)

Colorless Solid (278 mg). IR (ATR): $\tilde{\nu}$ = 3185 (w), 1647 (w), 1464 (vs), 1422 (vs), 1401 (vs), 1287 (vs), 1269 (vs), 1182 (m), 1164 (m), 1138 (w), 1099 (w), 1036 (w), 1016 (vs), 916 (w), 868 (m), 770 (m), 751 (w), 736 (w) cm^{-1}. EA ($CCdN_6O_2$): calculated C 4.99, H 0.0, N 34.95 %; found C 4.56, H 1.33, N 28.51 %. DSC ($5\,°\text{C}\,\text{min}^{-1}$): T_d = 326 °C.

Mercury 5-nitriminotetrazolate hydrate (101)

Colorless solid (317 mg). IR (ATR): $\tilde{\nu}$ = 3442 (w), 1626 (w), 1489 (s), 1418 (s), 1361 (s), 1324 (vs), 1284 (vs), 1185 (w), 1119 (w), 1028 (m), 953 (w), 870 (w), 757 (w), 730 (w), 700 (w) cm^{-1}. DSC ($5\,°\text{C}\,\text{min}^{-1}$): T_d = 184 °C.

Dithallium(I) 5-nitriminotetrazolate (102)

Pale yellow solid (345 mg, 6.43 µmol, 64 %). IR (ATR): $\tilde{\nu}$ = 1471 (w), 1430 (s), 1373 (s), 1338 (vs), 1266 (vs), 1112 (s), 1098 (s), 1051 (m), 1013 (m), 999 (s), 851 (s), 752 (m), 727 (m) cm^{-1}. EA ($CN_6O_2Tl_2$): calculated C 2.24, H 0.0, N 15.66 %; found C 2.15, H 0.0, N 15.43 %. DSC ($5\,°\text{C}\,\text{min}^{-1}$): T_d = 302 °C.

Lead 5-nitriminotetrazolate (103)

Colorless solid (268 mg). IR (ATR): $\tilde{\nu}$ = 3441 (w), 1504 (w), 1448 (s), 1385 (vs), 1355 (vs), 1295 (vs), 1216 (w), 1151 (m), 1132 (m), 1086 (w), 1014 (s), 869 (m), 805 (m), 749 (s), 725 (m) cm^{-1}. EA (CN_6O_2Pb): calculated C 3.58, H 0.0, N 25.07 %; found C 2.61, H 0.0, N 18.46 %. DSC ($5\,°\text{C}\,\text{min}^{-1}$): T_d = 290 °C.

Dicopper(I) 5-nitriminotetrazolate hydrate (104)

A solution of 5-nitrimino-1,4*H*-tetrazole (130 mg, 1.00 mmol) in water (3 mL) and sodium hydroxide solution (2 M, 1 mL) was added to copper(II) chloride dihydrate (341 mg, 2.00 mmol) in water (14 mL) at 80 °C. The resulting blue-green suspension was heated to 90 °C and sodium ascorbate (198 mg, 1.00 mmol) in water (1 mL) was added drop wise. The now bright yellow suspension was refluxed for 15 minutes, cooled down to room temperature and filtered. The residue was washed with water and ethanol to yield a dark green solid (253 mg). IR (ATR): $\tilde{\nu}$ = 3301 (m), 2359 (w), 2104 (w), 1624 (m), 1482 (s), 1365 (s), 1297 (vs), 1258 (s), 1191 (m), 1021 (w), 924 (w), 872 (w), 733 (w) cm^{-1}. EA ($CCu_2N_6O_2$): calculated C 4.71, H 0.0, N 32.94 %; found C 5.07, H 1.91, N 28.75 %. DSC (5 $°\text{C min}^{-1}$): T_d = 219 °C. Sensitivities (grain size < 100 µm): IS 10 J, FS 30 N.

Summary and Conclusions

The general goal of this thesis has been the synthesis of new nitrogen-rich primary explosives with the main focus on the azido-1,2,4-triazole system. Additionally, some other systems based on azido-1,2,3-triazole, tetrazole and nitrimino-1,2,4-triazole were also investigated.

Chapter 2 The already described, yet poorly characterized 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**), as well as several new metal and nitrogen-rich salts with sodium (**5**), potassium (**6**), cesium (**7**), silver (**8**), lead (**9**), ammonium (**10**), guanidinium (**11**) and aminoguanidinium (**12**) were synthesized and comprehensively characterized. Single crystal X-ray diffraction was used to reveal the structure of several of the investigated compounds, including the title compound **3**. Unfortunately, the thermal stabilities turned out to be rather low (mostly around 140 °C). While the nitrogen-rich salts were all found to be insensitive towards external stimuli, the opposite is true for the metal salts. Using the Microtox® method, **3** and **6** were proven to be less toxic to the marine bacterium *Aliivibrio fischeri* than RDX. By virtue of their capability to undergo a DDT upon slow heating, the potassium (**3**), cesium (**7**), silver (**8**) and lead (**9**) salts qualify as primary explosives. The initiation capability of the potassium salt **6** was positively tested with RDX.

Chapter 3 The novel compound 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**15**) was synthesized and comprehensively characterized for the first time. The reactivity of the nitrile was demonstrated by the reaction with hydroxylamine, forming 3-azido-1*H*-1,2,4-triazole-5-carboxamidoxime (**16**). The amine was successfully exchanged with a chloride upon diazotation in hydrochloric acid, resulting in 5-azido-1*H*-1,2,4-triazole-3-carbohydroximoyl chloride (**17**). All three neutral compounds (**15**, **16**, **17**) were investigated by single crystal X-ray diffraction, revealing interesting structural motifs. It was shown that compounds **15** and **16** are both able to form their silver salts **18** and **19**, respectively. The thermal stability of all five compounds **15–19** is in the vicinity of 165 °C. The neutral compounds exhibit moderate sensitivities while the two silver salts have to be classified as very sensitive. Unfortunately, only **18** detonated upon slow heating and neither of the two silver salts detonated upon rapid heating.

Chapter 4 The rather low thermal stabilities of **3** and **15** and their salts prompted the utilization of a tetrazole instead of a nitro or cyano group. Thus, a synthetical procedure based on reported reactions was developed for 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**20**). Several salts with silver (**21**), copper(I) (**22**), potassium (**23**, **25**), cesium (**24**), copper(II)

(**26**), ammonium (**27**, **31**), hydrazinium (**28**), guanidinium (**29**, **32**) and aminoguanidinium (**30**) were prepared and comprehensively characterized. The use of single crystal X-ray diffraction (**20**, **23** $\cdot$ H_2O, **24**, **25** $\cdot$ $3\,H_2O$, **27**) revealed the higher acidity of the tetrazole bonded hydroxyl group, thus explaining the vastly improved thermal stabilities of the salts with the monovalent anion. The latter mostly turned out to be much more stable than neutral **20**, while the salts with the bivalent anion display stabilities roughly equal to **20**. The salts range from extremely sensitive metal-based primary explosives (**21**, **23**–**26**) to insensitive nitrogen-rich compounds (**27**, **29**, **31**, **32**). It was shown that most of the metal salts are capable of a DDT upon slow heating, but only the silver salt **21** detonated when heated rapidly. Nevertheless, the initiation capability of the potassium salt **23** was still positively tested with RDX.

Chapter 5 Another option besides a 1-hydroxytetrazole, as utilized in **20**, would be a regular unsubstituted tetrazole. Thus, several salts of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) with silver (**34**), copper(I) (**35**), potassium (**36**, **38**), cesium (**37**, **39**), copper(II) (**40**), ammonium (**41**, **43**) and guanidinium (**42**, **44**) were prepared and well characterized. The structure of **37** was determined by low-temperature single crystal X-ray diffraction, again proving the higher acidity of the tetrazole ring. The thermal stabilities approximately match those of **20** and its salts. Sensitivities turned out to be comparable as well, ranging once more from extremely sensitive metal-based primary explosives (**34** and **36**–**40**) to insensitive nitrogen-rich compounds (**41**–**44**). Except for **35**, all of the metal salts are capable of a DDT when heated slowly but, in contrast to and as an improvement on previous compounds, also when heated rapidly by a hot needle (**34**, **36** and **38**–**40**).

Chapter 6 The second possibility to introduce a tetrazole functionality comes in the form of a C-N connection of the two rings, motivating the preparation and characterization of 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**49**). While regrettably incurring the disadvantage of preventing the deprotonation of the tetrazole instead of the triazole moiety, which was previously discovered to greatly benefit the thermal stability, the, for this chapter distinctive, C-N link allows studying any potential stabilizing effects of a neutral tetrazole substituent on the 1,2,4-triazolate, similar to those provided by nitro and cyano groups. Unfortunately, preparation of the silver salt did not succeed, so the capability to form ionic primary explosives could not be investigated. Interestingly, the decomposition onsets for the isomers **33** and **49**, and also the hydroxy analogue **20**, were all measured at around 150 °C, with almost identical values. This seems to indicate that the linkage to the azide is apparently even weaker than that to the C-N bonded tetrazole.

Chapter 7 Several silver salts of mostly already known azido-1,2,4-triazoles with different substituents were prepared, in order to investigate their capability as primary explosives. The chosen substituents were hydrogen (**50**), a second 5-azido-1*H*-1,2,4-triazole (**53**), amine (**57**), nitrimine (**58**), carboxamide (**61**) and methyl (**64**). Additionally, the two new compounds 3-azido-1*H*-1,2,4-triazole-5-carboxamide (**61**) and 2-(3-azido-1*H*-1,2,4-triazol-5-yl)acetic acid (**66**) were successfully synthesized for the first time. While the neutral compounds generally display a rather moderate thermal stability in the vicinity 140 °C, the novel **61** decomposes at 202 °C, which is the best thermal stability of all neutral azidotriazoles described in the study at hand. Except for **61** and **64** all of the neutral compounds have to be classified as highly sensitive to impact and friction. Except for one (**62**), all the silver salts are deemed true primary explosives which undergo a DDT upon slow heating and in the majority of cases also upon rapid heating. Unfortunately, the silver salts are in every case except for 3-azido-5-nitrimino-1,4*H*-1,2,4-triazole (**58**) less thermally stable than the parent neutral molecule.

Chapter 8 The novel compounds 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**72**) and 5-(5-nitro-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**73**) were successfully synthesized and thoroughly characterized. Although **72** features a 1,2,3-triazole, its decomposition temperature of 152 °C is identical to the ones of 1,2,4-triazole derivatives **33** and **49**. The metal salts with potassium (**76**), cesium (**77**) and silver (**75**) are all true primary explosives and capable of a fast DDT when heated both slowly as well as rapidly, or even when directly burned. The silver salt **75** is an extremely friction sensitive compound and should be handled with utmost care. These salts are more potent primary explosives than those of **33** or its hydroxy derivative **20**, which did not detonate upon burning. The initiation capability of the cesium salt **77** was positively tested with RDX. Unfortunately, all salts are even less thermally stable than the parent compound, and also it was not possible to obtain suitable single crystals for X-ray diffraction to determine the site of deprotonation. The detonation parameters of the three neutral compounds with an amino (**71**), azido (**72**) or nitro (**73**) group were additionally calculated using EXPLO5. Despite high enthalpies of formation all three compounds show inferior performance than RDX, mainly due to their lower densities.

Chapter 9 The synthesis of 5-(tetrazol-1-yl)-2*H*-tetrazole (**79**) was slightly optimized and various new metal and nitrogen-rich salts with silver (**80**), copper(I) (**81**), cesium (**83**), hydroxylammonium (**84**) and triaminoguanidinium (**85**) were prepared. Both the silver (**80**) as well as the copper(I) (**81**) salt are true primary explosives capable of a DDT even upon rapid heating. Unfortunately, the latter already decomposes at 128 °C. The salts with non-toxic potassium (**82**) and cesium (**83**) cations also showed potential primary explosive capabilities, but only as long as they are in anhydrous form. Unfortunately, both rehydrated over time. The calculated detonation parameters (EXPLO5) of **84** and **85** reveal them as inferior to RDX due to their low densities.

Chapter 10 Several transition metal salts of 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole), bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane and 5-nitrimino-1,4*H*-tetrazole with manganese, chromium, iron, cobalt, nickel, copper, zinc, silver, cadmium, mercury, thallium and lead were prepared and investigated as potential primary explosives with facile syntheses. Unfortunately, almost all compounds are hydrates and proper dehydration was unsuccessful. The few anhydrous exceptions to this contain either expensive or toxic cations (silver, thallium, lead), which served only as comparison regarding performance and thermal stability. While the salts of 5,5′-dinitrimino-3,3′-bis(1,4*H*-1,2,4-triazole) and bis(5-nitrimino-1,4*H*-1,2,4-triazol-3-yl)methane (**87**–**93**) display on average rather moderate thermal stabilities and are no primary explosives, those of 5-nitrimino-1,4*H*-tetrazole (**94**–**104**) show mostly excellent thermal stabilities and are all except for one (the thallium salt **102**) capable of a DDT when heated slowly. Unfortunately, only the water free silver (**99**) and lead (**103**) salts detonated when heated rapidly.

General Conclusion and Outlook In essence, it can be concluded that azido-1,2,4-triazoles have the capability to form capable primary explosives, even with alkali metals like potassium. Unfortunately, the salts of azidotriazoles which feature an electron withdrawing group (nitro, cyano, nitrimino, etc.) as second substituent typically improved upon the thermal stabilities of the corresponding neutral compounds only by a small margin. On the other hand, the salts of azidotriazoles instead featuring an electron donating or neutral group (hydrogen, carboxamido, etc.) decomposed at even lower temperatures than their corresponding neutral molecules. This problem could be circumvented by the introduction of a deprotonatable C-C linked tetrazole derivative, stabilizing the system by getting deprotonated first, due to its higher acidity. This general problem concerning the stability of a neutral compound versus its anion, depending on the substituent, would be an interesting topic for future theoretical and experimental investigations. Nevertheless, some of the compounds, especially the potassium (**6**) and cesium (**7**) salts of 5-azido-3-nitro-1*H*-1,2,4-triazole (**3**) and the cesium salt **37** of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole (**33**) might be worthwhile investigating, in terms of their use as potential sensitizers in priming mixtures, for example. The important properties (enthalpies and energies of formation, thermal stability, sensitivities, capability to undergo a DDT) of all the investigated azido-1,2,4-triazoles of this thesis are compiled in table 11.1 and are sorted with increasing energy of formation per kilogram of material.

Table 11.1: Compilation of the investigated azido-1,2,4-triazoles and their corresponding silver salts. The highly dangerous 3,5-diazido-1H-1,2,4-triazole (DAzT) is added as comparison.[158] An asterisk indicates a new compound.

	Formula	$\Delta_f U°_{(s)}$ / kJ kg^{-1}	$\Delta_f H°_{(s)}$ / kJ mol^{-1}	T_m / °C	T_d / °C	IS / J	FS / N	ESD / mJ	DDT [a]	fast heating [b]
61 *	$C_3H_3N_7O$	1585.3	229.1		202	40	360	100		
62 *	$C_3H_2AgN_7O$				132	5	4	15	no	def.
16 *	$C_3H_4N_8O$	2681.8	434.7		158	10	240	—		
19 *	$C_3H_3AgN_8O$				166	3	24	10	no	def.
3	$C_2HN_7O_2$	3104.5	469.0	110	149	5	42	50		
8 *	$C_2AgN_7O_2$				149	1	5	3	yes	det.
58	$C_2H_2N_8O_2$	3138.6	519.0		121	2	7	40		
59 *	$C_2HAgN_8O_2$				141	1	20	30	yes	det.
64	$C_3H_4N_6$	3264.8	392.8	136	156	40	160	1000		
	$C_3H_3AgN_6$ [c]				—	—	—	—	(yes)	(def.)
57	$C_2H_3N_7$	3643.7	443.4		131	5	192	100		
	$C_2H_2AgN_7$ [c]				—	—	—	—	(yes)	(def.)
20 *	$C_3H_2N_{10}O$	4179.1	795.1	83	144	4	120	260		
21 *	$C_3HAgN_{10}O$				184	1	5	5	yes	det.
50	$C_2H_2N_6$	4222.1	454.8	113	139	4	192	200		
51	C_2HAgN_6				129	1	5	12	yes	det.
33	$C_3H_2N_{10}$	4460.2	779.5		152	1	20	50		
34 *	C_3HAgN_{10}				180	1	5	14	yes	det.
53	$C_4H_2N_{12}$	4551.4	975.5		181	3	48	40		
54 *	$C_4Ag_2N_{12}$				148	1	5	12	yes	det.
15 *	C_3HN_7	4624.6	614.8	114	161	25	160	500		
18 *	C_3AgN_7				171	2	16	18	yes	def.
49 *	$C_3H_2N_{10}$	4675.2	817.8		152	4	10	100		
	C_3HAgN_{10}				—	—	—	—	—	—
DAzT	C_2HN_9	5355.2	796.7	100	122	< 1	< 5	7		
	C_2AgN_9				(120 [d])	—	—	—	—	—

[a] Slow heating on a spatula; [b] hot needle or direct burning; [c] compound could not be obtained pure; [d] sodium salt.[158]

Appendix

A.1 Abbreviations and Formula Symbols

Abbreviations

BAM	*Bundesanstalt für Materialforschung und -prüfung*
BNCP	tetraammine-*cis*-bis(5-nitrotetrazolato-N^2)cobalt(III) perchlorate
br	broad (IR and NMR)
CL-20	2,4,6,8,10,12-hexanitrohexaazaisowurtzitane
d	doublet (NMR)
DBX-1	copper(I) 5-nitrotetrazolate
DDNP	2-diazo-4,6-dinitrophenol
DDT	detonation-to-deflagration transition
DEI	direct electron ionization
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EA	elemental analysis
EBW	exploding bridgewire
ESD	electrostatic discharge
FAB	fast atom bombardment
FOX-7	1,1-diamino-2,2-dinitroethene
FS	friction sensitivity
HMX	high melting explosive (1,3,5,7-tetranitro-1,3,5,7-tetrazocane)
HTPB	hydroxyl-terminated polybutadiene
IR	infrared spectroscopy
IS	impact sensitivity
KDNP	potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan
LA	lead azide
LS	lead styphnate
$[M]^+$	molecule peak (MS)
M	molar ($\mathrm{mol\,L^{-1}}$)
m	medium (IR), multiplet (NMR)
MF	mercury fulminate
MMH	monomethylhydrazine

MS	mass spectrometry
NBO	natural bond orbital
NMR	nuclear magnetic resonance
PETN	pentaerythritol tetranitrate
ppm	parts per million
RDX	royal demolitions explosive (1,3,5-trinitro-1,3,5-triazinane)
s	strong (IR), singlet (NMR)
SII	simple initiating impulse
TATB	2,4,6-triamino-1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TTA	2,4,6-triazido-1,3,5-triazine
t	triplet (NMR)
UN	United Nations
vs	very strong (IR)
vw	very weak (IR)
w	weak (IR)

Formula Symbols

δ	isotropic chemical shift
D	detonation velocity
^{n}J	coupling constant over n nuclei
m/z	mass per charge
M	molar mass
N	nitrogen content
n	amount of substance
$\tilde{\nu}$	wave number
Ω	oxygen balance
p_{CJ}	detonation pressure
Q_{v}	heat of explosion
ρ	density
T_{d}	decomposition temperature
T_{dh}	dehydration temperature
T_{ex}	explosion temperature
T_{m}	melting temperature
V_{0}	volume of detonation gases

A.2 Crystal Structure of RDX at 100 and 173 K

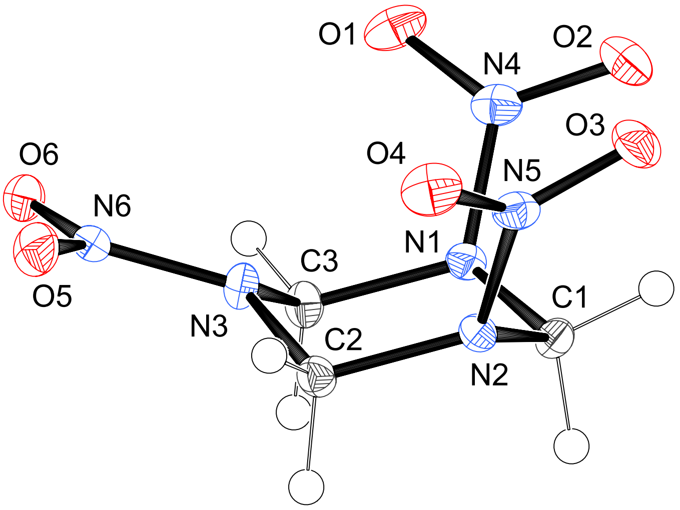


Figure A.1: Molecular structure of RDX at 100 K with a calculated density of $1.841\,\mathrm{g\,cm^{-3}}$. Thermal ellipsoids at 50 % probability.

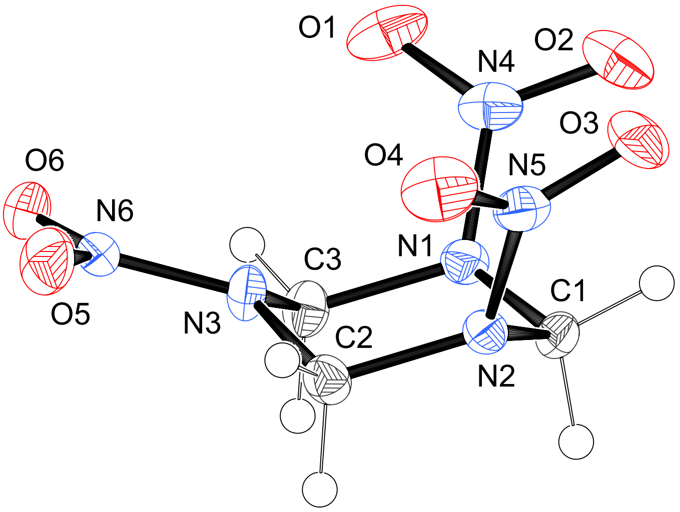


Figure A.2: Molecular structure of RDX at 173 K with a calculated density of $1.824\,\mathrm{g\,cm^{-3}}$. Thermal ellipsoids at 50 % probability.

A.3 Crystallographic Data

Table A.1: Crystallographic data for **3**, **4** and **6**.

	3	**4**	**6**
Measurement	gx679	hx157	hx068
Sum formula	$C_2HN_7O_2$	$C_3H_3N_7O_2$	$C_2KN_7O_2$
Formula moiety	$C_2HN_7O_2$	$C_3H_3N_7O_2$	$C_2KN_7O_2$
M / $\mathrm{g\,mol^{-1}}$	155.10	169.12	193.19
Color	colorless	colorless	yellow
Habit	block	needle	needle
Crystal size / mm	0.40 × 0.30 × 0.15	0.40 × 0.05 × 0.03	0.35 × 0.10 × 0.05
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pnma$ (62)	$P2_1/m$ (11)	$P2_1/c$ (14)
a / Å	10.4057(8)	6.9585(16)	4.4403(2)
b / Å	5.8792(6)	5.9641(13)	11.8862(4)
c / Å	9.4946(8)	8.5356(16)	12.7766(6)
α / °	90	90	90
β / °	90	106.59(2)	100.167(4)
γ / °	90	90	90
V / Å^3	580.85(9)	339.49(12)	663.74(5)
Z	4	2	4
$\rho_{\mathrm{calc.}}$ / $\mathrm{g\,cm^{-3}}$	1.774	1.654	1.933
T / K	173(2)	173(2)	173(2)
$F(000)$	312	172	384
μ / $\mathrm{mm^{-1}}$	0.156	0.141	0.768
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-13 \leq h \leq 13$	$-8 \leq h \leq 8$	$-5 \leq h \leq 5$
	$-7 \leq k \leq 7$	$-7 \leq k \leq 6$	$-14 \leq k \leq 14$
	$-11 \leq l \leq 12$	$-9 \leq l \leq 10$	$-15 \leq l \leq 15$
θ range / °	4.29–27.49	4.23–27.00	4.66–26.00
Collected reflections	3230	1927	6582
Independent reflections	732	805	1307
Observed reflections	555	625	1132
R_{int}	0.0314	0.0216	0.0268
Parameters	70	73	109
Restraints	0	0	0
Data-to-parameter ratio	10.5	11	12
Hydrogen atom treatment	refall	constr	—
R_1 (all data)	0.0443	0.055	0.0283
R_1 (obs.)	0.0309	0.0407	0.0215
wR_2 (all data)	0.0873	0.1161	0.0527
wR_2 (obs.)	0.0772	0.1078	0.0503
S	1.034	1.082	1.041
Res. dens. min. / e Å^{-3}	−0.238	−0.241	−0.157
Res. dens. max. / e Å^{-3}	0.144	0.311	0.227
Solution	SIR97	SIR97	SIR97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
CCDC number	871252	875278	871253

Table A.2: Crystallographic data for **9**, **15** and **16**.

	9	**15**	**16**
Measurement	hx263	hx341	hx415
Sum formula	$C_4H_2N_{14}O_5Pb$	C_2HN_7	$C_3H_4N_8O$
Formula moiety	$C_4H_2N_{14}O_5Pb$	C_2HN_7	$C_3H_4N_8O$
M / g mol^{-1}	533.39	135.11	168.14
Color	yellow	colorless	colorless
Habit	block	block	block
Crystal size / mm	0.20 × 0.20 × 0.05	0.40 × 0.40 × 0.30	0.20 × 0.15 × 0.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)
a / Å	19.4348(4)	5.7067(4)	10.616(3)
b / Å	8.7495(2)	5.0156(4)	7.3524(19)
c / Å	15.6181(4)	19.4844(15)	9.8450(19)
α / °	90	90	90
β / °	105.429(2)	96.687(7)	112.78(3)
γ / °	90	90	90
V / Å^3	2560.06(10)	553.90(7)	708.5(3)
Z	8	4	4
$\rho_{\text{calc.}}$ / g cm^{-3}	2.768	1.62	1.576
T / K	173(2)	173(2)	298(2)
$F(000)$	1968	272	344
μ / mm^{-1}	13.245	0.124	0.128
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-23 \leq h \leq 23$ $-10 \leq k \leq 10$ $-19 \leq l \leq 19$	$-6 \leq h \leq 7$ $-5 \leq k \leq 6$ $-18 \leq l \leq 24$	$-12 \leq h \leq 12$ $-7 \leq k \leq 8$ $-7 \leq l \leq 11$
θ range / °	4.32–26.00	4.20–25.98	4.49–25.49
Collected reflections	24771	2721	2595
Independent reflections	4996	1085	1306
Observed reflections	4357	927	1002
R_{int}	0.0539	0.0218	0.0247
Parameters	449	95	125
Restraints	4	0	0
Data-to-parameter ratio	11.1	11.4	10.5
Hydrogen atom treatment	mixed	refall	refall
R_1 (all data)	0.0313	0.0412	0.0607
R_1 (obs.)	0.0251	0.033	0.0426
wR_2 (all data)	0.0595	0.0896	0.1042
wR_2 (obs.)	0.0563	0.083	0.0908
S	1.115	1.051	1.066
Res. dens. min. / e Å^{-3}	−1.188	−0.209	−0.201
Res. dens. max. / e Å^{-3}	2.462	0.149	0.134
Solution	SIR97	SIR97	SIR97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
CCDC number	917586	917716	917717

Table A.3: Crystallographic data for **17** $\cdot \frac{1}{2}$ EtOH, **20** and **23** $\cdot$ H_2O.

	17 $\cdot \frac{1}{2}$ EtOH	**20**	**23** $\cdot$ H_2O
Measurement	hx539	ix027	ix125
Sum formula	$C_8H_{10}Cl_2N_{14}O_3$	$C_3H_4N_{10}O_2$	$C_3H_3KN_{10}O_2$
Formula moiety	$2\,(C_3H_2ClN_7O)$, C_2H_6O	$C_3H_2N_{10}O$, H_2O	$C_3H_3KN_{10}O_2$
M / g mol^{-1}	421.2	212.16	250.25
Color	colorless	colorless	colorless
Habit	block	block	block
Crystal size / mm	0.05 × 0.05 × 0.40	0.40 × 0.21 × 0.12	0.328 × 0.169 × 0.147
Crystal system	triclinic	triclinic	triclinic
Space Group	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a / Å	7.5886(5)	7.3393(8)	5.4113(3)
b / Å	9.5569(6)	7.3888(10)	7.7578(5)
c / Å	12.3612(8)	7.8723(9)	11.4883(6)
α / °	86.564(5)	97.515(10)	97.343(5)
β / °	83.608(5)	95.120(9)	103.252(5)
γ / °	75.727(5)	98.213(10)	108.526(6)
V / Å^3	862.91(10)	416.35(9)	434.46(4)
Z	2	2	2
$\rho_{\mathrm{calc.}}$ / g cm^{-3}	1.621	1.692	1.913
T / K	173(2)	173(2)	100(2)
$F(000)$	428	216	252
μ / mm^{-1}	0.423	0.143	0.620
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-9 \leq h \leq 9$	$-8 \leq h \leq 9$	$-6 \leq h \leq 6$
	$-11 \leq k \leq 11$	$-8 \leq k \leq 9$	$-9 \leq k \leq 9$
	$-15 \leq l \leq 13$	$-7 \leq l \leq 9$	$-14 \leq l \leq 14$
θ range / °	4.28–26.00	4.29–26.00	4.15–26.00
Collected reflections	5881	2174	6298
Independent reflections	3304	1618	1707
Observed reflections	2778	1409	1590
R_{int}	0.0225	0.0145	0.0246
Parameters	265	152	157
Restraints	0	0	0
Data-to-parameter ratio	12.5	10.6	10.1
Hydrogen atom treatment	mixed	refall	refall
R_1 (all data)	0.0434	0.041	0.0260
R_1(obs.)	0.0342	0.0344	0.0237
wR_2 (all data)	0.086	0.0924	0.0583
wR_2 (obs.)	0.0804	0.085	0.0569
S	1.034	1.034	1.080
Res. dens. min. / e Å^{-3}	−0.297	−0.212	−0.290
Res. dens. max. / e Å^{-3}	0.383	0.268	0.259
Solution	SIR97	SIR97	SIR97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
CCDC	917718	926338	926339

Table A.4: Crystallographic data for **24**, **25** $\cdot$ 3 H_2O and **27**.

	24	**25** $\cdot 3\,H_2O$	**27**
Measurement	hx563	ix004	ix007
Sum formula	$C_3HCsN_{10}O$	$C_3H_6K_2N_{10}O_4$	$C_3H_7N_{11}O_2$
Formula moiety	$C_3HCsN_{10}O$	$C_3H_6K_2N_{10}O_4$	$C_3HN_{10}O$, H_2O, H_4N
M / g mol^{-1}	326.05	324.38	229.2
Color	colorless	colorless	colorless
Habit	plate	block	block
Crystal size / mm	0.30 × 0.25 × 0.03	0.330 × 0.141 × 0.044	0.280 × 0.153 × 0.133
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a / Å	9.1227(5)	7.0409(5)	6.5687(5)
b / Å	13.2619(8)	9.3509(8)	8.0401(5)
c / Å	7.2375(4)	10.0485(8)	9.9620(7)
α / °	90	110.164(7)	108.599(6)
β / °	103.866(6)	108.102(7)	104.990(6)
γ / °	90	97.863(6)	99.305(6)
V / Å^3	850.11(8)	567.81(8)	464.23(6)
Z	4	2	2
$\rho_{\text{calc.}}$ / g cm^{-3}	2.548	1.897	1.640
T / K	173(2)	100(2)	100(2)
$F(000)$	608	328	236
μ / mm^{-1}	4.349	0.868	0.138
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-11 \leq h \leq 11$ $-15 \leq k \leq 15$ $-8 \leq l \leq 8$	$-8 \leq h \leq 8$ $-11 \leq k \leq 11$ $-12 \leq l \leq 12$	$-8 \leq h \leq 8$ $-10 \leq k \leq 10$ $-12 \leq l \leq 12$
θ range / °	4.23–26.00	4.27–25.99	4.21–26.37
Collected reflections	5089	5754	6732
Independent reflections	1622	2229	1882
Observed reflections	1225	1802	1615
R_{int}	0.047	0.0374	0.029
Parameters	136	196	173
Restraints	0	0	0
Data-to-parameter ratio	11.9	11.4	10.9
Hydrogen atom treatment	constr	refall	refall
R_1 (all data)	0.0489	0.0442	0.0385
R_1 (obs.)	0.0327	0.0312	0.0311
wR_2 (all data)	0.0835	0.0731	0.0839
wR_2 (obs.)	0.0712	0.0673	0.0783
S	1.038	1.025	1.036
Res. dens. min. / e Å^{-3}	−0.788	−0.278	−0.208
Res. dens. max. / e Å^{-3}	1.468	0.304	0.255
Solution	SIR97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
CCDC	921798	921799	929865

Table A.5: Crystallographic data for $\mathbf{37} \cdot \frac{2}{3}\,H_2O$, $\mathbf{50} \cdot H_2O$ and **66**.

	37	**50**	**66**
Measurement	ix005	jx383	jx390
Sum formula	$C_9H_6Cs_3N_{30}O_2$	$C_2H_4N_6O$	$C_4H_6N_6O_3$
Formula moiety	$C_9H_6Cs_3N_{30}O_2$	$C_2H_2N_6$, H_2O	$C_4H_4N_6O_2$, H_2O
M / g mol^{-1}	965.17	128.11	186.15
Color	colorless	colorless	colorless
Habit	block	rod	block
Crystal size / mm	0.346 × 0.111 × 0.077	0.424 × 0.130 × 0.099	0.346 × 0.111 × 0.077
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$(2)	$Pna2_1$ (33)	$P2_1/c$ (14)
a / Å	10.3681(4)	13.8179(7)	4.7911(3)
b / Å	10.9931(5)	10.2561(5)	12.0043(6)
c / Å	13.7281(6)	4.0300(2)	13.0591(7)
α / °	69.963(4)	90	90
β / °	69.799(4)	90	91.894(5)
γ / °	87.218(3)	90	90
V / Å^3	1375.24(11)	571.12(5)	750.67(7)
Z	2	4	4
$\rho_{\text{calc.}}$ / g cm^{-3}	2.331	1.490	1.647
T / K	100(2)	173(1)	173(1)
$F(000)$	902	264	384
μ / mm^{-1}	4.028	0.123	0.141
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-12 \leq h \leq 12$ $-13 \leq k \leq 13$ $-16 \leq l \leq 16$	$-17 \leq h \leq 16$ $-10 \leq k \leq 12$ $-5 \leq l \leq 4$	$-4 \leq h \leq 5$ $-15 \leq k \leq 15$ $-16 \leq l \leq 15$
θ range / °	4.20–26.00	4.239–26.364	4.256–26.371
Collected reflections	13916	4065	5169
Independent reflections	5383	1142	1516
Observed reflections	4514	1070	1302
R_{int}	0.0319	0.0219	0.0225
Parameters	420	98	142
Restraints	4	1	0
Data-to-parameter ratio	12.8	11.7	10.7
Hydrogen atom treatment	mixed	refall	refall
R_1 (all data)	0.0425	0.0254	0.0382
R_1 (obs.)	0.0329	0.0229	0.0312
wR_2 (all data)	0.0862	0.0559	0.0827
wR_2 (obs.)	0.08	0.0545	0.0774
S	1.065	1.072	1.045
Res. dens. min. / e Å^{-3}	−0.809	−0.131	−0.170
Res. dens. max. / e Å^{-3}	1.819	0.096	0.178
Solution	SIR97	SHELXS-2013	SHELXS-2013
Refinement	SHELXL-97	SHELXL-2013	SHELXL-2013
CCDC	926996	1402896	1402897

Table A.6: Crystallographic data for **70**, **84** and **85**.

	70	**84**	**85**
Measurement	jx203	hx308	ix028
Sum formula	$C_{10}H_{11}N_5O$	$C_2H_5N_9O$	$C_3H_{10}N_{14}$
Formula moiety	$C_{10}H_{11}N_5O$	C_2HN_8, H_4NO	$C_2H_1N_8$, CH_9N_6
M / g mol^{-1}	217.23	171.15	242.25
Color	colorless	colorless	colorless
Habit	block	plate	rod
Crystal size / mm	0.267 × 0.127 × 0.117	0.30 × 0.20 × 0.05	0.46 × 0.13 × 0.11
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$ (14)	$Pbca$ (61)	$P2_12_12_1$ (19)
a / Å	11.731(4)	7.1205(5)	4.0843(8)
b / Å	7.423(2)	9.9489(7)	14.1931(17)
c / Å	11.188(4)	20.5644(14)	17.696(3)
α / °	90	90	90
β / °	93.655(3)	90	90
γ / °	90	90	90
V / Å^3	972.3(5)	1456.81(18)	1025.8(3)
Z	4	8	4
$\rho_{\text{calc.}}$ / g cm^{-3}	1.484	1.561	1.569
T / K	173(2)	173(2)	173(2)
$F(000)$	456	704	504
μ / mm^{-1}	0.104	0.129	0.123
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-14 \leq h \leq 14$ $-9 \leq k \leq 9$ $-12 \leq l \leq 13$	$-8 \leq h \leq 8$ $-12 \leq k \leq 12$ $-25 \leq l \leq 25$	$-4 \leq h \leq 5$ $-17 \leq k \leq 16$ $-11 \leq l \leq 22$
θ range / °	4.14–26.37	4.21–26.00	4.46–26.37
Collected reflections	6884	13407	5473
Independent reflections	1980	1427	2077
Observed reflections	1738	1213	1627
R_{int}	0.0235	0.0405	0.036
Parameters	189	129	194
Restraints	0	0	0
Data-to-parameter ratio	10.5	11.1	10.7
Hydrogen atom treatment	mixed	refall	refall
R_1 (all data)	0.0376	0.0372	0.0554
R_1 (obs.)	0.0318	0.0295	0.0368
wR_2 (all data)	0.0802	0.0838	0.0711
wR_2 (obs.)	0.0758	0.0788	0.0647
S	1.063	1.098	0.99
Res. dens. min. / e Å^{-3}	−0.203	−0.162	−0.156
Res. dens. max. / e Å^{-3}	0.24	0.175	0.138
Solution	SIR97	SIR97	SIR97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
CCDC	1406925	901937	920718

Table A.7: Crystallographic data for **92** · 2 H_2O, RDX (100 K) and RDX (173 K).

	92 · 2 H_2O	RDX (100 K)	RDX (173 K)
Measurement	gx635	ix090	ix091
Sum formula	$C_5H_{16}N_{10}NiO_{10}$	$C_3H_6N_6O_6$	$C_3H_6N_6O_6$
Formula moiety	$C_5H_{12}N_{10}NiO_8$, 2 H_2O	$C_3H_6N_6O_6$	$C_3H_6N_6O_6$
M / g mol^{-1}	434.99	222.14	222.14
Color	green	colorless	colorless
Habit	block	block	block
Crystal size / mm	0.35 × 0.34 × 0.30	0.40 × 0.40 × 0.25	0.40 × 0.40 × 0.25
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pnma$ (62)	$Pbca$ (61)	$Pbca$ (61)
a / Å	9.7191(7)	11.4545(5)	11.5100(5)
b / Å	14.6069(12)	10.6169(5)	10.6532(5)
c / Å	11.0803(8)	13.1773(6)	13.1969(6)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V / Å^3	1573.0(2)	1602.51(13)	1618.18(13)
Z	4	8	8
$\rho_{\text{calc.}}$ / g cm^{-3}	1.837	1.841	1.824
T / K	173(2)	100(2)	173(2)
$F(000)$	896	912	912
μ / mm^{-1}	1.312	0.175	0.173
Absorption correction	multi-scan	multi-scan	multi-scan
Index range	$-12 \leq h \leq 8$ $-13 \leq k \leq 18$ $-14 \leq l \leq 10$	$-11 \leq h \leq 14$ $-9 \leq k \leq 13$ $-16 \leq l \leq 13$	$-11 \leq h \leq 14$ $-10 \leq k \leq 13$ $-16 \leq l \leq 13$
θ range / °	4.23–27.00	4.33–26.00	4.31–25.99
Collected reflections	8405	3936	4095
Independent reflections	1778	1562	1581
Observed reflections	1489	1344	1358
R_{int}	0.0394	0.0225	0.0203
Parameters	165	136	136
Restraints	0	0	0
Data-to-parameter ratio	10.8	11.5	11.6
Hydrogen atom treatment	mixed	constr	constr
R_1 (all data)	0.0409	0.0374	0.0399
R_1 (obs.)	0.0302	0.0307	0.033
wR_2 (all data)	0.0770	0.0836	0.0906
wR_2 (obs.)	0.0703	0.0782	0.0833
S	1.081	1.095	1.09
Res. dens. min. / e Å^{-3}	−0.387	−0.244	−0.238
Res. dens. max. / e Å^{-3}	0.495	0.222	0.195
Solution	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
CCDC	1402898	927275	927276

A.4 List of Publications

Peer-reviewed Publications

- Dániel Izsák, Thomas M. Klapötke, Characterization of the Energetic Plasticizer Methyl-NENA, *Z. Anorg. Allg. Chem.* **2011**, *637*, 2135–2141.
- Niko Fischer, Dániel Izsák, Thomas M. Klapötke, Sebastian Rappenglück, Jörg Stierstorfer, Nitrogen-Rich 5,5′-Bistetrazolates and their Potential Use in Propellant Systems: A Comprehensive Study, *Chem. Eur. J.* **2012**, *18*, 4051–4062.
- Dániel Izsák, Thomas M. Klapötke, Preparation and Crystal Structure of 5-Azido-3-nitro-1*H*-1,2,4-triazole, Its Methyl Derivative and Potassium Salt, *Crystals* **2012**, *2*, 294–305.
- Dániel Izsák, Thomas M. Klapötke, Stephan Reuter, Thomas Rösener, Silver Salt and Derivatives of 5-Azido-1*H*-1,2,4-triazole-3-carbonitrile, *Z. Anorg. Allg. Chem.* **2013**, *639*, 899–905.
- Niko Fischer, Dániel Izsák, Thomas M. Klapötke, Jörg Stierstorfer, The Chemistry of 5-(Tetrazol-1-yl)-2*H*-tetrazole: An Extensive Study of Structural and Energetic Properties, *Chem. Eur. J.* **2013**, *19*, 8948–8957.
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