Selective Synthesis and Characterization of the Highly Energetic Materials 1-Hydroxy-5H-tetrazole (CHN₄O), its Anion 1-Oxido-5H-tetrazolate (CN₄O⁻) and Bis(1-hydroxytetrazol-5-yl)triazene

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Abstract: For the first time, an adequate selective synthesis, circumventing the formation of 2-hydroxy-5H-tetrazole, of 1-hydroxy-5H-tetrazole (HTO), as well as the synthesis of bis(1-hydroxytetrazol-5-yl)triazene (H₂T) are reported. Several salts thereof were synthesized and characterized which resulted in the formation of new primary and secondary explosives containing the 1-oxidotetrazolate unit. Molecular structures are characterized by single-crystal X-ray diffraction, H and ¹³C NMR, IR, and elemental analysis. Calculation of the detonation performance using the EXPLO5 code confirmed the energetic properties of 1-hydroxy-5H-tetrazole. The detonation properties can be adjusted to the requirements for those of a secondary explosive by forming the hydroxylammonium (6) or hydrazinium (7) salts, or to meet the requirements of a primary explosive by forming the silver salt 4, which shows a fast DDT on contact with a flame. The sensitivities of all compounds towards external stimuli such as impact, friction, and electrostatic discharge were measured.

Introduction

Tetrazoles are a class of heterocycles that exhibit a wide variety of possible applications. A prominent representative is Losartan, which is included in the WHO’s List of Essential Medicines as a treatment for hypertension. In addition to pharmaceutical uses, tetrazoles show great potential for application as energetic materials with high nitrogen contents like in copper(I) nitrotetrazolate (DBX-1). The high endothermic heat of formation of tetrazoles (e.g., +236 kJ mol⁻¹ for 1,5H-tetrazole) is advantageous for possible applications as energetic materials, since a large amount of energy is released upon detonation. General protocols to further increase the enthalpy of formation of tetrazoles include N-oxidation by Oxone®, HOF, or H₂O₂, which also has the advantage of increasing the oxygen balance of tetrazoles. Since a large amount of energy is released upon detonation, general protocols to further increase the enthalpy of formation of tetrazoles include N-oxidation by Oxone®, HOF, or H₂O₂, which also has the advantage of increasing the oxygen balance of tetrazoles. In 2012, Klapótke et al. obtained dihydroxylammonium-5,5'-bistetrazol-1,1'-dial (TKX-50) through the N-oxidation of 5,5'-bistetrazole followed by formation of the hydroxylammonium salt. This compound possesses excellent detonation properties while being thermally stable (221 °C) and moderately sensitive towards impact (20 J) and friction (120 N), thus being stable enough to be safely used as a high-performing secondary explosive. TKX-50 surpasses properties of 1,3,5-Trinitro-1,3,5-triazinan (RDX) and 1,3,5,7-Tetranitro-1,3,5,7-tetrazocan (HMX), which have long been used as the main charge in detonation devices. Even though the 5,5'-bistetrazole has been known since 1892, it took nearly 100 years until its potential for use as an explosive was discovered in the compound TX-50. It is therefore surprising that 1,5H-tetrazole has been known since 1892, but complete characterization of the corresponding N-oxide, namely 1-hydroxy-5H-tetrazole, is missing.

The first synthesis was reported by Pallazzo in 1910 (Figure 1), however, the addition of hydrazic acid to sodium fulminate is not suitable nor desired for a synthesis on gram-scale due to the high risks involved when working with fulminates. In 1956, Bettini et al. successfully synthesized 1-hydroxy-5H-tetrazole by the addition of hydrazic acid to nitrolic acids, which too is not desired for the work on gram-scale. Bettini et al. also described the silver salt of 1-hydroxytetrazole, yet an extensive characterization is missing. In 1995, Begtrup et al. used Oxone® to oxidize 1,5H-tetrazole. This idea was then followed by Giles et al. in 1999 for oxidizing ethyl tetrazole-5-carboxylate. Both procedures result in an isomeric mixture of the 1-hydroxy- and 2-hydroxytetrazole derivatives, requiring further protection (for the oxidized 1H-tetrazole), as well as separation of the isomers and subsequent secession of the protecting group. In a previous paper in 2013, we showed that the addition of hydroxylamine to a solution of cyanogen azide results in a cyclization forming 5-amino-1-hydroxytetrazole (5-ATO). In 1954, Henry et al. showed that 1,5H-tetrazole can be obtained by the elimination of the amino group of 5-amino-1H-tetrazole through diazotization followed by subsequent reduction of the diazonium cation. These so-called hydro-dediazoniations are performed by boiling a diazonium cation in acidic ethanol. However, this procedure usually results in ethoxy-dediazoniation. Kornblum et al. later replaced the step in which reduction with acidic ethanol occurs...
by using hypophosphorous acid as the reducing agent instead.\[19\]

Independently from the applied reduction procedure, the dediazonization always starts with a diazotization of the amine, which, for several azoles, can instantly explode and therefore should never be isolated. It can also couple with other compounds and this well-known behavior is exploited to produce azo dyes, such as Methyl red (2-(N,N-dimethyl-4-aminophenyl))\[20\] or Tartrazine (trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate).\[21\] Lesser known are triazenes, which result from the coupling of a diazonium cation with an amine. In 1910 Hofmann et al. published the first synthesis of sodium bis(tetrazol-5-yl)triazene by diazotization of amino guanidinium nitrate with sodium nitrite, intermediately producing 5-aminotetrazole which then further reacts to the triazene species.\[22\]

When applying the systems analogously to 5-ATO, the dediazonization selectively produces 1-hydroxy-5H-tetrazole, thus representing the first adequate selective synthesis for this long over-due compound, whereas following Hofmann et al. results in the formation of bis(1-hydroxytetrazol-5-yl)triazene, the twice N-oxidized bis(tetrazol-5-yl)triazene. Therefore, we report the first adequate procedure to obtain 1-hydroxy-5H-tetrazole without the need of protection groups and elaborate workups. Additionally, the first synthesis of bis(1-hydroxytetrazol-5-yl)triazene is reported. Both acids as well as salts thereof are prepared and are characterized by single crystal X-ray diffraction experiments, complemented by NMR and IR spectrometry as well as thermal and physical analysis.

**Results and Discussion**

**Synthesis**

*Warning! The synthetic work described in this section involves the handling of very sensitive intermediates (diazotetrazole-1 N-oxide) and products (e.g., silver salt 4). Proper protective measurements and equipment must be used!*

The starting material 5-ATO is readily available from the reaction of cyanogen azide and hydroxylamine.\[17\] 1-Hydroxy-5H-tetrazole (1) can be obtained by dissolving 5-ATO in semi-concentrated sulfuric acid (40%) and diazotizing with sodium nitrite, while keeping the temperature below 5°C (Scheme 1). The diazotization solution is then added to a mixture of ethanol and elemental copper and stirred at 55°C for 2 hours. Due to the intermediate formation of 5-diazonium-1-hydroxytetrazole, 4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate).\[21\] The synthetic work described in this section involves the handling of very sensitive intermediates (diazotetrazole-1 N-oxide) and products (e.g., silver salt 4). Proper protective measurements and equipment must be used!

![Scheme 1. Synthesis of 1-hydroxy-5H-tetrazole (1) and its salts thereof (2–7), as well as the synthesis of bis(1-hydroxytetrazol-5-yl)-triazene (8) and its salts thereof (9–15). Hx⁺: hydroxylammonium; Hz⁺: hydrazinium; G⁺: guanidinium.](image-url)
the ratio of 5-ATO to sulfuric acid (40%) should be quite low. A ratio of 1:10 was used for the synthesis of all herein investigated compounds, as a higher concentration of 5-diazonium-1-hydroxytetrazole leads to micro-detonations within the reaction solution. An attempt to reduce the amount of acid to a ratio of 1:2 resulted in a violent detonation of the whole reaction solution, destroying the round-bottom flask. Compound 1 was extracted into DCM, and the ammonium salt (5) was subsequently precipitated by passing gaseous ammonia through the organic phase. The sodium (2) and potassium (3) salts were obtained by refluxing a solution of the corresponding carbonate and 5 in water, followed by evaporating to complete dryness, extracting the residue with ethanol, and precipitating the salts by adding diethyl ether. The silver salt (4) can be precipitated by adding silver nitrate to a solution of 1 in water and filtering off the solid. The hydrazinium (6) and hydradzinum (7) salts were obtained by adding the corresponding base to a solution of 1 in ethanol and precipitating with diethyl ether. Due to coextraction of sulfuric acid after dediazonization pure 1 is obtained by dissolving 3 in 2 M hydrochloric acid, extracting with ethyl acetate, and removing the solvent in vacuo. Bis-(1-hydroxytetrazol-5-yl)triazene 8 was obtained as a monohydrate by dissolving 5-ATO in concentrated hydrochloric acid followed by diazotization with half an equivalent of sodium nitrite, adjusting to pH >10 with sodium hydroxide, and extraction into ethyl acetate. The copper ammonium salt 15 was obtained by precipitating the copper salt of 8 using copper sulfate followed by recrystallization from concentrated ammonia.

When preparing compound 8, it is important to make sure any trace amounts of the diazonium cation are removed by stirring under basic conditions (pH >10), since it is possible to co-extract it into the organic solvent. When removing the solvent in vacuo, a detonation occurred on slightly touching the solid with a plastic spatula, leading to the person performing the experiment being injured.

Crystal structures

The solid-state crystal structure of all of the compounds synthesized in this work, except compound 14, were determined using low-temperature single-crystal X-ray diffraction. All of the data and parameters of the measurements, as well as of the refinements are given in the Supporting Information Table S1. All crystal densities are recalculated to their respective room temperature crystal density. Crystal datasets were deposited in the CSD database and can be obtained free of charge with the following codes: CCDC 2088975 (1), 2088974 (2a), 2088980 (2b), 2088977 (3), 2088979 (4), 2088985 (5), 2088982 (6), 2088986 (7), 2088988 (8), 2088983 (9), 2088978 (10), 2088976 (11), 2088975 (12), 2088981 (13) and 2088984 (15). 1-Hydroxy-SH-tetrazole (1) crystallizes in the monoclinic space group P2₁/n. The density of (1) (1.63 g cm⁻³) is comparable to that of the parent molecule 5-amino-1-hydroxytetrazole (1.66 g cm⁻³) and is significantly higher than that of 1-aminotetrazole (1-AT, 1.48 g cm⁻³). Figure 2 shows the crystal structure of 1, which forms wave-like layers in an AB₆ layering (along the b and c-axis) due to the two H atoms present per molecule participating in a total of three hydrogen bonds to two different 1-hydroxy-SH-tetrazole molecules – one of which lies within the same wave-like layer (A), whereas the other is from a different layer (B) (Figure 2B).

Interestingly, the respective C–N and N–N bond lengths within the tetrazole ring are nearly equivalent for compound 1 compared to 5-ATO and 1-AT. The bond length between the hydroxy group and the tetrazole ring in 1 is the same as that reported for 5-ATO, but is slightly shorter than the corresponding bond of the amine in 1-AT, thus explaining the higher density. All of the bond lengths are in the typical range for N–N, C–N, and N–O single bonds, as well as N–N and C–N double bonds. The tetrazole ring in 1 is planar, with the oxygen atom slightly protruding from the plane (O1–N1–N2–N3 = 5°).

In all of the salts of 1 investigated in this work, a planar arrangement of the oxygen atom with respect to the tetrazole plane was observed for the 1-oxido-SH-tetrazolate anions.

Sodium 1-oxido-SH-tetrazolate (2) crystallizes as a monohydrate in two polymorphs, one in the triclinic space group P1 (2a) with a density of 1.81 g cm⁻³ and one in the orthorhombic space group P2₁2₁2 (2b) with a slightly lower density of 1.78 g cm⁻³. The triclinic form is obtained by crystallization from water, whereas the orthorhombic polymorph from ethanol. Deprotonation of 1 results in marginal changes in the bond lengths of the tetrazole ring, with the N1–O1 bond length being generally shortened by 0.03–0.04 Å for all investigated salts in comparison with the neutral compound 1. Potassium (3) and silver 1-oxido-SH-tetrazolate (4) both crystallize in the orthorhombic space group Pnma, with densities of 1.88 g cm⁻³.
bond lengths [Å] and angles [°] for the ammonium cation with four distinct tetrazolate anions. Selected hydrogen due to the presence of hydrogen bonds between the hydrogen atoms of an ammonium cation (Figure 4), with bonds towards three oxygen atoms and one nitrogen atom of four different 1-oxidotetrazolate anions. The observed density is the lowest of all of the herein investigated compounds, and remarkably, it is even lower than that of comparable compounds such as ammonium 1-oxido-5-aminotetrazolate (1.50 g cm⁻³) and ammonium 5-azidotetrazolate (1.61 g cm⁻³).[24]

Hydroxylammonium 1-oxido-5H-tetrazolate (6) crystallizes in the triclinic space group P1 with a density of 1.67 g cm⁻³ (298 K) with one molecular unit in the unit cell as shown in Figure 5. Although all of the protons participate in hydrogen bonds, the density of 6 is significantly lower than that of comparable molecules such as dihydroxylammonium dinitro-bis-1,2,4-triazole-1,1’-dil (MAD-X1) (1.90 g cm⁻³ at 298 K)[10] or TXK-50 (1.92 g cm⁻³ at 298 K).[10]

The lower density is also indicated by a lower packing coefficient[25] (Figure 6) of 6 (0.752) compared to TKX-50 (0.811) and MAD-X1 (0.797). Interestingly, the packing coefficient of 6 is comparable to the hydroxylammonium salt of 5-ATO (0.762) but is significantly higher than that for 1,HH-tetrazole (0.675). This confirms the positive effect of N-oxidation on the density as stated by Fischer et al.[12] whereas amination at the carbon position does not lead to significant changes in density.

![Figure 3](image3.png)

Figure 3. Crystal structure of silver 1-oxido-5H-tetrazolate showing the coordination environment of the silver cations. Selected bond distances [Å]: N4···Ag1: 2.235(3), N3···Ag1: 2.753(3), O1···Ag1: 2.628(8), O1’···Ag1’: 2.406(7); angles [°]: O1’···Ag1-N4 124.97(12), N3···Ag1-N4 122.14(11), O1’···Ag1-N3’ 81.73(12); Symmetry codes: i) x+y, 1/2-z, ii) y, x, z, iii) -x, y, -z.

![Figure 4](image4.png)

Figure 4. Packing of ammonium 1-oxido-5H-tetrazolate (5) showing layering due to the presence of hydrogen bonds between the hydrogen atoms of an ammonium cation with four distinct tetrazolate anions. Selected hydrogen bond lengths [Å] and angles [°] for D–H···A, d(H···A), d(D–H···A), < (D–H···A); N5–H5B···O1: 0.93(2), 1.86(2), 2.7762(18), 172(2); N5–H2–O1: 0.91(2), 1.90(2), 2.8036(19), 171(2); N5–H5–O1: 0.90(3), 2.04(3), 2.9063(18), 162(2); N5–H4–N3: 0.88(3), 2.18(2), 2.9762(18), 151(2). Symmetry codes: i) 1/2 + x, 1/2 - y, z; ii) x, 1 + y, z; iii) 1-x, 1-y, -1/2 + z.

![Figure 5](image5.png)

Figure 5. A) Crystal structure of hydroxylammonium 1-oxidotetrazolate (6). B) Packing due to the presence of strong hydrogen bonds involving all of the protons. Selected bond lengths [Å]: O1–N1 1.319(2), N1–N2 1.343(3), N2–N3 1.304(3), N3–N4 1.350(3), N4–C1 1.328(3), C1–N1 1.332(3), N5–O2 1.411(2); Angles [°]: O1–N1–N2 122.13(2), N1–N2–N3 106.19(18), N2–N3–N4 110.74(18), N3–N4–C1 105.86(18), N4–C1–N1 108.36(18), C1–N1–O1 129.02(18); Selected bond angles [°] for D–H···A, d(D–H), d(D···H), d(H···A), < (D–H···A); O2–H2–O1: 0.82(4), 1.76(4), 2.57(2), 172(4); C1–H1–O2: 0.92(3), 2.57(3), 3.27(2), 134(2); N5–H5 A···N3: 0.81(3), 2.18(3), 2.913(3), 151(3); N5–H5B···N4: 0.84(3), 2.05(3), 2.883(3), 170(3); N5–S C···O1: 0.88(3), 1.93(3), 2.7662(18), 160(3). Symmetry codes: i) –1 + x, 1+y, z; ii) x; iii) 1-x, 1+y, z; iv) –1 + x, –1 + z.
Generally, it can be assumed that the introduction of a bicycle (TKX-50, MADE-X-1) is beneficial as it increases the packing coefficient, and thus increases the density.

Hydrazinium 1-azonio-5H-tetrazolate (7) crystallizes in the monoclinic space group $Pc$ with two molecular units in the unit cell and a density of 1.6 g cm$^{-3}$, following the trend observed of hydrazinium salts having lower densities compared to the corresponding hydroxylammonium salts. The crystal structure of 7 is shown in Figure 7A, in which all hydrogen atoms are participating in hydrogen bonds resulting in one $\text{N}_4\text{H}_4^+$ cation being linked to four anions (Figure 7B).

Bis-(1-hydroxytetrazol-5-yl)triazene (8) crystallizes in the monoclinic space group $P2_1/n$ as a monohydrate with a density of 1.80 g cm$^{-3}$ and four molecular units in the unit cell (Figure 8). Due to the high acidity of the hydroxy group next to the azo-moiety, 8 crystallizes in a zwitterionic form where one tetrazole ring (N4) is protonated by its own hydroyx group (O1). While the self-protonation only leads to small differences in bond lengths between the two 1-hydroxytetrazol units, changes in bond angles between the two moieties of up to 4.7° (N3–N4–C1 = 109.4(2), N10–N11–C2 = 104.7(1)) are observed. The largest difference in bond lengths and angles is observed for the triazene bridge. Within the triazene bridge, the N5–N6 bond (1.269(2) Å) is significantly shorter than the N6–N7 bond (1.327(2) Å), suggesting a higher bond order and therefore more double bond character for the N5–N6 bond. Additionally, the zwitterionic ring is more strongly bent towards the triazene bridge (N6–N5–C1 = 107.9(1)°) than its counterpart (N6–N7–C2 = 114.8(1)°). Compounds 9 and 10 both crystallize as hexahydrates in the triclinic space group $P1$ with a density of 1.67 g cm$^{-3}$ and 1.71 g cm$^{-3}$, respectively. Tripotassium bis(1-azonio-5-yl)triazenide (11) crystallizes as a trihydrate in the orthorhombic space group $P2_12_12_1$ with a density of 1.309(3) Å in 11. The most drastic change in the structure of the anion resulting from complete deprotonation of 8 doesn’t appear to lead to significant changes in bond lengths within the tetrazole rings, the double bond character of the N5–N6 bond in the triazene-bridge has now been more delocalized, which is indicated by the equality of the N5–N6 and N6–N7 bond lengths which are both 1.309(3) Å in 11.

Compounds 12 and 13 both crystallize as trihydrates. It was not possible to obtain crystals of compound 14 suitable for single crystal X-ray diffraction experiments. The crystal structures of compounds 9, 10, 12 and 13 are shown in the Supporting Information (Figures S1-S4).

Ammonium copper bis(1-azonio-5-yl)triazenide (15) crystallizes in the triclinic space group $P1$ with two molecular

**Figure 7.** A) Crystal structure of hydrazinium 1-azonio-5H-tetrazolate (7, 8). B) Packing due to strong hydrogen bonds of all protons, linking four distinct anions by one hydrazinium cation. Selected bond lengths [Å]: O1–N1 1.329(3), N1–N2 1.338(3), N2–N3 1.316(4), N3–N4 1.344(4), N4–C1 1.329(4), C1–N1 1.329(4), N5–N6 1.443(4); Angles [°]: O1–N1–N2 120.8(2), N1–N2–N3 105.7(2), N2–N3–N4 111.0(3), N3–N4–C1 105.6(3), N4–C1–N1 108.6(3), C1–N1–O1 130.1(3); Selected hydrogen bond lengths [Å] and angles [°]: H5B···O1: 0.89(4), 2.45(4), 170(3), N6 bond. Additionally, the zwitterionic ring is more strongly bent towards the triazene bridge (N6–N5–C1 = 107.9(1)°) than its counterpart (N6–N7–C2 = 114.8(1)°). Compounds 9 and 10 both crystallize as hexahydrates in the triclinic space group P1-1 with a density of 1.67 g cm$^{-3}$ and 1.71 g cm$^{-3}$, respectively. Tripotassium bis(1-azonio-5-yl)triazenide (11) crystallizes as a trihydrate in the orthorhombic space group $P2_12_12_1$ with two molecular

**Figure 8.** Crystal structure of bis(1-hydroxytetrazol-5-yl)triazene monohydrate (8), showing the zwitterionic form. Selected bond lengths [Å]: O1–N1 1.329(2), N1–N2 1.349(2), N2–N3 1.338(2), N4–C1 1.337(2), C1–N5 1.368(2), N5–N6 1.269(2), N6–N7 1.317(2), N7–C2 1.368(2), N10–N11 1.361(2), N12–N13 1.316(2), N13–N14 1.316(2), N14–C1 1.337(2), C1–N5 1.368(2), N5–N6 1.269(2), N6–N7 1.317(2), N7–C2 1.368(2), N10–N11 1.361(2), N12–N13 1.316(2), N13–N14 1.316(2), N14–C1 1.337(2), C1–N5 1.368(2), N5–N6 1.269(2), N6–N7 1.317(2), N7–C2 1.368(2), N10–N11 1.361(2), N12–N13 1.316(2), N13–N14 1.316(2), N14–C1 1.337(2), C1–N5 1.368(2), N6–C1 107.9(1), C2–N7–N6 114.8(1).

**Figure 9.** Crystal structure of tripotassium bis(1-azonio-5-yl)triazenide trihydrate (11). Selected bond lengths of the anion [Å]: O1–N1 1.330(3), N1–N2 1.352(4), N2–N3 1.311(3), N3–N4 1.339(3), N4–C1 1.340(4), C1–N1 1.339(4), C1–N5 1.384(4), N5–N6 1.309(3), N6–N7 1.309(3), N7–C2 1.375(4), C2–N8 1.346(4), N8–O2 1.330(3), N8–N9 1.346(2), N9–N10 1.316(4), N10–N11 1.359(3), N11–C2 1.340(4); Angles [°]: O1–N1–N2 121.8(1), O1–N1–C1 128.3(1), O2–N8–N9 123.5(1), O2–N8–C2 126.6(1), N3–N4–C1 109.4(2), N10–N11–C2 104.7(1), C1–N5–N6 107.9(1), C2–N7–N6 114.8(1).
units in the unit cell and a density of 1.96 g cm\(^{-3}\) (Figure 10). As was observed for compound 11, the bond lengths and angles of the anion are not significantly influenced by deprotonation. The drastic conformational change observed in 11 is a result of the unequal coordination of the copper(II)-cation with the two 1-oxidotetrazolate moieties. Whereas the most favored conformation for compounds 8–14 is apparently a triazene bridge with a double (E)- arrangement along N5–N6 and N6–N7, threefold coordination of the copper(II) cation by the anion in 15 results in rotation along the N6–N7 bond, resulting in a \(\text{E/Z}\) conformation along N5–N6 and N6–N7, respectively. Interestingly, the copper(II) cation shows a nearly perfectly square pyramidal coordination by the anion and two aqua ligands. The angles involving O3 and atoms forming the equatorial plane (O1, N8, N11, O4) range from 89.13° (O1–Cu1–O3) to 104.42° (O3–Cu1–N11).

NMR spectroscopy

NMR spectroscopy was performed in DMSO-\(d_6\), D\(_2\)O or acetone-\(d_6\) and spectra are depicted in the Supporting Information. The \(^1\)H NMR spectrum of compound 1 in DMSO-\(d_6\) shows one signal at \(\delta = 9.48\) ppm for the proton attached to the carbon atom of the tetrazole ring. The \(^{13}\)C NMR of compound 1 in DMSO-\(d_6\) shows one signal at \(\delta = 137.7\) ppm, which is shifted upfield compared to the starting material 5-ATO (\(\delta = 150.5\) ppm). Deprotonation of 1 leads to a shift in the signals observed in the \(^1\)H as well as \(^{13}\)C NMR spectra. For example, the \(^1\)H NMR of potassium 1-oxido-5H-tetrazolate (3) in D\(_2\)O shows one signal at \(\delta = 8.54\) ppm, which is shifted upfield compared to the free acid 1. Additionally, the signal in the \(^{13}\)C NMR of 3 in D\(_2\)O is shifted downfield to \(\delta = 164.5\) ppm. The \(^{13}\)C NMR of compound 8 in DMSO-\(d_6\) shows one signal at \(\delta = 150.0\) ppm. The carbon atoms of 8 are, contrary to 1, not drastically shifted. Deprotonation of 8 results in a downfield shift of the signal. The \(^{13}\)C NMR of the tripotassium salt (11) in D\(_2\)O shows one signal at \(\delta = 153.2\) ppm. The influence of deprotonation of 8 on the \(^{13}\)C NMR signal is not as prominent as that observed for compound 1.

**Physicochemical properties**

**Thermal behavior.** The thermal behaviors of compounds 1–7 are shown in Figure 12. Compound 1 shows a decomposition temperature of 186 °C (Figure 12), and two endothermic events at 80 °C and 96 °C, which TGA indicates as corresponding to a phase transition and/or melting point. Compound 1, 1-hydroxy-5H-tetrazole, exhibits a higher thermal stability compared to the similar compound 5-amino-1-hydroxytetrazole (105 °C), and is almost identical with that of 1-aminitetrazole (182 °C).

Compound 2 shows loss of water at 110 °C and a decomposition temperature of 273 °C, which is the highest of all of the 1-hydroxy-5H-tetrazole salts reported in this work (Figure 12). The potassium (3) and the silver (4) salts, which are both free of water, show decomposition temperatures of 236 °C and 211 °C, respectively. Both of these salts detonate violently on reaching their critical temperatures. The silver salt (4) also immediately detonates on contact with a flame. Compound 5 shows an endothermic event at 180 °C, which corresponds to the loss of ammonia due to evaporation, as indicated by the onset of mass loss in the TG. The endothermic event seamlessly evolves into an exothermic decomposition at 188 °C, at which temperature a significant mass loss of 85.5 wt.% occurs as shown by the TG (Figure 12). The same behavior is observed for the hydroxyammonium salt 6. Figure 12 shows an endothermic event at 115 °C, which evolves into the first of two exothermic decomposition events at 159 °C. TGA measurements revealed the first decomposition to correspond to the decomposition of hydroxylamine accompanied by a weight loss of 24.9 wt.%. The second exothermic event with onset at 203 °C is attributed to the decomposition of the residual 1-hydroxy-5H-tetrazole.

Compound 7 shows an exothermic decomposition temperature of 213 °C, with two endothermic events in addition observed at 80 °C and 103 °C. The TG measurement of 7 shows
A mass loss of 13 wt.% with onset at 103°C, which corresponds to the evaporation of hydrazine. Therefore, it can be assumed that the exothermic event actually corresponds to thermal decomposition of residual neutral compound 1, rather than the hydrazinium salt itself. Figure 13 shows that bis-(1-hydroxytetrazol-5-yl)triazene monohydrate (8) is thermally stable up to 95°C. Despite being a monohydrate, no endothermic event which could be attributed to a loss of water was observed in the DTA spectrum of 8. Due to stabilization by crystal water, 8 decomposes immediately on reaching a temperature (95°C) high enough to remove the crystal water molecule. The alkaline salts 9–12 all show the presence of endothermic events between 85–135°C corresponding to the loss of water in each compound (Figure 13). In general, these compounds are very thermally stable, with decomposition temperatures of between 292°C (12) and 335°C (10). Interestingly, the triguanidinium salt 13 shows no endothermic event in the DTA, which confirms loss of water already occurring at room temperature. This agrees with the measured elemental analysis, which fits perfectly with the values calculated for the anhydrous salt, which shows a thermal stability of up to 222°C. The hydroxylammonium salt 14 shows an endothermic event at 104°C which evolves into an exothermic decomposition, a behavior similar to that of compound 5 (Figure 12). This can be explained by the evaporation of hydroxylamine occurring, which results in the formation of an unstable residue that immediately decomposes at 148°C. Interestingly, compound 15 shows no loss of water until the onset of decomposition at 198°C, indicating strong coordinative bonds of the aqua ligands to the copper(II) cation as well as a high stability of the crystal water.

Heats of formation, sensitivity, and detonation parameters. The calculated and measured explosive properties of all compounds are listed in Tables 1 and 2. Heat of formations were calculated by applying the atomization method using room temperature CBS-4 M enthalpies. A detailed explanation of the calculation can be found in the Supporting Information. Compound 1 shows a comparable heat of formation (252 kJ mol⁻¹) to its parent molecule 5-amino-1-hydroxytetrazole (256 kJ mol⁻¹). However, 1 possesses a slightly lower density than its parent compound, which results in a...
Table 1. Energetic properties of 1-hydroxy-5H-tetrazole (1) and its salts 2–7.

| 1 | 2a | 2b | 3 | 4 | 5 | 6 | 7 |
|---|----|----|---|---|---|---|---|
| Formula | CH₃NOH | CH₃NOHNa | CH₃NOHNa | CH₃NOHNa | CH₃NOHAg | CH₃NO₂ | CH₃NO₂ | CH₃NO₂ |
| M (g mol⁻¹) | 86.05 | 126.05 | 126.05 | 124.14 | 189.21 | 103.09 | 119.08 | 118.10 |
| ΔV (kJ mol⁻¹) | 10 | > 40 | > 40 | 4 | < 1 | > 40 | 6 | 26 |
| FS [kJ mol⁻¹] | 28 | > 360 | > 360 | 54 | 1 | > 360 | 240 | > 360 |
| ΔH₂⁰ [kJ mol⁻¹] | 160 | 1080 | 1080 | 63 | < 0.28 | > 1500 | > 1500 | 740 |
| Δn [kJ kg⁻¹] | 3.47 | 4.10 | 4.70 | 1.67 | 1.60 | 1.91 | 1.91 | 1.91 |
| ρ (g cm⁻³) | 65.11 | 44.45 | 45.13 | 29.04 | 67.94 | 58.81 | 71.16 | 37.84 |
| TS₀ [°C] | −18.59 | −12.36 | −12.36 | −32.22 | −8.29 | −38.80 | −20.15 | −40.64 |
| ΔH₀ [kJ mol⁻¹] | −37.19 | −25.39 | −25.39 | −45.11 | −16.59 | −54.33 | −33.59 | −54.19 |
| Δn₀ [kJ kg⁻¹] | 188.6 | 273 | 273 | 236 | 211 | 188 | 159.23 | 213 |
| ΔH₀/K [kJ mol⁻¹] | 252 | −3 | −366 | −364 | 47 | −207 | 259 | 346 |
| ν₀ (m s⁻¹) | 3042 | −2803 | −2780 | 441 | 2170 | 2325 | 3100 | 369 |

Table 2. Energetic properties of bis-(1-hydroxytetrazol-5-yl)triazene monohydrate (8) and its salts 9–15.

| 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|
| Formula | CH₃NOH | CH₃NOH | CH₃NOH | CH₃NOH | CH₃NOH | CH₃NOH | CH₃NOH |
| M (g mol⁻¹) | 234.14 | 339.01 | 387.16 | 381.45 | 520.55 | 390.34 | 312.22 |
| ΔV (kJ mol⁻¹) | 18 | 1.67 | 1.67 | 1.97 | 2.55 | 1.59 | 1.97 |
| FS [kJ mol⁻¹] | 66.66 | 45.45 | 39.80 | 40.39 | 29.60 | 71.77 | 62.81 |
| ΔH₂⁰ [kJ mol⁻¹] | −10.38 | −7.08 | −6.20 | −25.17 | −9.22 | −49.19 | −15.37 |
| Δn [kJ kg⁻¹] | −24.23 | −16.52 | −14.46 | −33.56 | −15.37 | −69.69 | −25.62 |
| TS₀ [°C] | 100 | 311 | 339 | 294 | 292 | 222 | 146 |
| ΔH₀/K [kJ mol⁻¹] | 734 | −1505 | −450 | −1475 | −158 | 464 | 53 |
| Δn₀ [kJ kg⁻¹] | 3248 | −4303 | −3705 | −3786 | −559 | 1633 | −38 |
| ν₀ (m s⁻¹) | 8405 | 7555 | 7428 | 7056 | 8013 | 9284 | 9437 |

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] From X-ray diffraction analysis recalculated to 298 K. [d] Nitrogen content. [e] Oxygen balance towards CO formation. [f] Oxygen balance towards CO₂ formation. [h] Temperature of endothermic event (DTA; β = 5 °C min⁻¹). [i] Temperature of exothermic event (DTA; β = 5 °C min⁻¹). [j] Calculated enthalpy of formation. [k] Calculated mass related enthalpy of formation. [l] Energy of explosion. [m] Detonation temperature. [n] Volume of detonation products (assuming only gaseous products). [o] Detonation pressure at Chapman-Jouguet point. [p] Detonation velocity. [q] Values based on the Explo5 Database.

Minor reduction of the detonation velocity (8405 m s⁻¹) and detonation pressure (269 kbar) compared to 5-ATO (8609 m s⁻¹, 298 kbar). While the impact sensitivity of 1 (10 J) is comparable to that of 5-ATO (10 J), the friction sensitivity is higher for 1 (28 N) than for 5-ATO (108 N), meaning 1 is more sensitive towards external stimuli than 5-ATO. In contrast, the hydroxylammonium (6) salt of 1-hydroxy-5H-tetrazole shows a higher heat of formation (259 kJ mol⁻¹ (6)) compared to the corresponding salt of 5-ATO (Hx⁺: 227 kJ mol⁻¹). Compound 6 shows a very high detonation velocity (9284 m s⁻¹) compared to compound 5 (8013 m s⁻¹), which is due to the higher density of 6. 1.67 g cm⁻³ (5: 1.40 g cm⁻³). Although compound 7 shows a slightly lower density (1.60 g cm⁻³) than compound 6, the significantly higher enthalpy of formation of 7 (346 kJ mol⁻¹) results in its even higher detonation velocity of 9437 m s⁻¹. Compounds 6 and 7 both outperform even HMX in terms of detonation velocity. While compound 5 is completely insensitive (IS > 40 J, FS > 360 N), compounds 6 (IS = 6 J, FS 240 N) and 7 (IS = 26 J, FS > 360 N) show higher impact sensitivities, but crucially, are comparable to (6) or less sensitive (7) than HMX. The monohydrate sodium salt (2) is completely insensitive towards external stimuli, whereas the potassium (3) salt is more...
sensitive (IS = 4 J, FS = 54 N). The silver salt (4) is the most sensitive out of all of the compounds, and has to be classified as extremely sensitive, with an impact sensitivity below 1 J and a friction sensitivity of 1 N. The silver salt shows the characteristics of a primary explosive, immediately detonating on contact with a flame (Figure 14).

Due to this behavior, the initiation capability of 4 towards Pentaerythritol tetranitrate (PETN) was tested, whereby it was found that 50 mg of 4 were able to initiate 200 mg of pressed PETN (Figure 15). Compound 2a shows a low detonation velocity of 7555 m s⁻¹, which is attributed to its low heat of formation as well as being a monohydrate. The orthorhombic form 2b exhibits a slightly lower detonation velocity (7428 m s⁻¹) than triclinic 2a, due to the lower density of 2b. Interestingly, the potassium salt 3 exhibits an even lower detonation velocity than 2a/b, even though it has a higher density (1.88 g cm⁻³). Due to the high heat of formation of compound 8 (734 kJ mol⁻¹), it shows an outstanding detonation velocity of 9433 m s⁻¹, as well as a very high detonation temperature (3940 K), which even outperforms HMX. However, in addition to its low thermal stability (decomposition temperature of only 100 °C), compound 8 is also very sensitive towards impact (< 1 J) and friction (4 N), preventing application of 8 as a high-performance secondary explosive.

Complete deprotonation of 8 forming the alkali salts 9 (Li⁺), 10 (Na⁺), and 11 (K⁺) results in a drastic decrease in energetic performance. This is due to the presence of a large amount of crystal water which results in highly exothermic enthalpy of formations (−1475−1505 kJ mol⁻¹). Additionally, the absence of protons, not included as crystal water, leads to a decrease in detonation velocity within the series of increasing cation weight. Compound 13, crystallizes as a trihydrate, but completely loses its crystal water by drying in air at room temperature, as confirmed by elemental analysis as well as IR spectroscopy. Therefore, the heat of formation and detonation properties were calculated for the anhydrous compound, showing an endothermic heat of formation (158 kJ mol⁻¹). The rather low density for 13 of 1.59 g cm⁻³, detonation velocity of 7870 m s⁻¹ and detonation pressure of 201 kbar means it lies in the range of the other alkali salts. Compound 14 was obtained as an amorphous solid which is thermally stable up to 146 °C. It has an endothermic heat of formation of 464 kJ mol⁻¹ and density of 1.79 g cm⁻³, with a calculated detonation velocity of 9663 m s⁻¹, which surpasses that of HMX. Compound 14 has a calculated detonation pressure of 364 kbar as well as moderate sensitivities to external sources (IS = 4 J, FS = 128 N), which are comparable to those of HMX.

**Conclusion**

For the first time, an adequate selective synthesis, circumventing the formation of 2-hydroxy-SH-tetrazole, of 1-hydroxy-SH-tetrazole is reported by the dediazonization of the readily available precursor, 5-amino-1-hydroxytetrazole. Diazotization was followed by reduction of the diazonium cation using either hypophosphorous acid or a mixture of ethanol/copper(0). While ethanol/copper(0) was inferior to hypophosphorous acid in terms of yields, this procedure was chosen for the synthesis of 1-hydroxy-SH-tetrazole (1), as it is far easier to workup. Diazotization of 5-ATO with half an equivalent of sodium nitrite resulted in the formation of bis(1-hydroxytetrazol-5-yl)triazene monohydrate (8). Compound 1 was converted to the sodium (2), potassium (3), silver (4), ammonium (5), hydroxylammonium (6) and hydrazinium (7) salts. Compound 8 was converted to the lithium (9), sodium (10), potassium (11), rubidium (12), guanidinium (13), hydroxylammonium (14), and ammonium copper(II) (15) salts. All compounds, except 14, were analyzed using single crystal X-ray diffraction, as well as NMR, IR, and EA analysis. The thermal stabilities were investigated, sensitivities towards external stimuli were determined, and the detonation performances were calculated using the EXPLO5 code. Compound 1 shows a good detonation performance (8405 m s⁻¹) which can compete with that of RDX. The detonation performance, thermal stability and sensitivities of 1 could be adjusted to meet the requirements of a primary explosive by formation of the silver salt (4), or to those of a highly energetic secondary explosive.
explosive by formation of 6 (VoD = 9284 m s\(^{-1}\)) or 7 (VoD = 9437 m s\(^{-1}\)), which surpass the detonation velocity of even HMX (9192 m s\(^{-1}\)). Bis(1-hydroxytetrazolyl)-5-sulfanilazene monohydrate (8) is a highly sensitive (IS < 1 J, FS = 4 N) material, with the performance of a high energetic secondary explosive (VoD = 9433 m s\(^{-1}\)). Salts of 8 are completely insensitive due to the incorporation of up to six equivalents of crystal water (for the lithium salt), which is accompanied by a drastic loss of performance.

The hydroxylammonium salt (14) is an anhydrous compound (as proven by elemental analysis), which shows a very high detonation velocity of 9633 m s\(^{-1}\) but with impact and friction sensitivities comparable to those of PETN (IS = 4 J, FS = 80 N).

**Experimental Section**

1-Hydroxy-5H-tetrazole (1): 5-Amino-1-hydroxytetrazole (1.00 g, 10 mmol) was dissolved in sulfuric acid (16 mL, 40%) and cooled to 0°C. 1-Hydroxytetrazole (4.85 mmol) was dissolved in water (10 mL) and potassium carbonate (670 mg, 4.85 mmol) was dissolved in water (10 mL) and potassium carbonate (670 mg, 4.85 mmol) was added. The solvent was completely dried off in air, and the solid obtained was extracted with hot ethanol and filtered. After recrystallization, potassium 1-oxido-5H-tetrazolate (3) was filtered off and obtained as a yellow powder in good yield (518 mg, 4.17 mmol, 86%). Crystals suitable for single crystal X-ray measurements were obtained by recrystallization from water.

1 H NMR (DMSO-d6, 25°C): \(\delta = 0.84\) ppm (s, 1H, CH); 13C NMR (DMSO-d6, 25°C): \(\delta = 135.1\) ppm (N4-C); IR (ATR, cm\(^{-1}\)): \(\nu = 3465\) (m), 3247 (m), 3281 (w), 3150 (m), 1652 (m), 1472 (m), 1433 (vw), 1407 (m), 1384 (w), 1350 (vw), 1309 (w), 1247 (s), 1192 (m), 1158 (w), 1114 (w), 1065 (w), 982 (w), 824 (m), 738 (m), 715 (w), 670 (m), 529 (s), 481 (vs); DTA (5°C min\(^{-1}\)): 236°C (\(T_{\text{onset}}\)); elemental analysis calcld [%] for CHAgN: 124.14; C 6.98, H 0.81, N 45.13; found: C 6.93, H 1.03, N 44.96; BAM drophammer: 4 J, BAM friction tester: 54 N, ESD: 63 mJ.

Silver 1-oxido-5H-tetrazolate (4): Compound 1 (150 mg, 1.74 mmol) was dissolved in ethanol (10 mL) and silver nitrate (296 mg, 1.74 mmol) was added. After stirring for several minutes, the precipitate was filtered off and washed with ethanol (10 mL) and diethyl ether (10 mL). Silver 1-oxido-5H-tetrazolate (4) was obtained as a white powder in quantitative yield (332 mg, 1.72 mmol, 99%). Crystals suitable for single crystal X-ray measurements were obtained by a three-layer diffusion crystallization over several days.

IR (ATR, cm\(^{-1}\)): \(\nu = 3100\) (m), 1454 (s), 1414 (s), 1340 (w), 1301 (w), 1246 (vs), 1206 (s), 1159 (m), 1108 (w), 1058 (w), 995 (w), 859 (s), 810 (w), 732 (s), 701 (m), 667 (m), 495 (s); DTA (5°C min\(^{-1}\)): 211°C (\(T_{\text{onset}}\)); elemental analysis calcld [%] for CHAgN (192.91): C 6.23, H 0.52, N 29.04; found: C 6.11, H 0.63, N 28.38; BAM drophammer: < 1 J, BAM friction tester: 1 N, ESD: < 0.28 mJ.

Ammonium 1-oxido-5H-tetrazolate (5): Compound 5 was obtained by passing gaseous ammonia through a solution of 1 in DCM/AgNO\(_3\). The precipitate in the DCM/AgNO\(_3\) solution was filtered off, extracted with methanol (40 mL), prior to diethyl ether being added. The precipitate was filtered off and dried in air. Ammonium 1-oxido-5H-tetrazolate (5) was obtained as an off-white powder in moderate yield (629 mg, 6.11 mmol, 61%). Crystals suitable for single crystal X-ray measurements were obtained by recrystallization from water.

1 H NMR (DMSO-d6, 25°C): \(\delta = 0.84\) ppm (s, 1H, CH); 13C NMR (DMSO-d6, 25°C): \(\delta = 135.1\) ppm (N4-C); IR (ATR, cm\(^{-1}\)): \(\nu = 3465\) (m), 3247 (m), 3281 (w), 3150 (m), 1652 (m), 1472 (m), 1433 (vw), 1407 (m), 1384 (w), 1350 (vw), 1309 (w), 1247 (s), 1192 (m), 1158 (w), 1114 (w), 1065 (w), 982 (w), 824 (m), 738 (m), 715 (w), 670 (m), 529 (s), 481 (vs); DTA (5°C min\(^{-1}\)): 188°C (\(T_{\text{onset}}\)); elemental analysis calcld [%] for CHN: 103.00; C 11.65, H 4.89, N 67.94; found: C 11.26, H 4.89, N 68.58; BAM drophammer: > 40 J, BAM friction tester: > 360 N, ESD: > 1500 mJ.

Hydroxylammonium 1-oxido-5H-tetrazolate (6): Compound 1 (500 mg, 5.81 mmol) was dissolved in ethanol (10 mL) and aqueous hydroxylamine solution (50%, 479 mg, 7.20 mmol) was added. After stirring for 5 minutes at 50°C, the precipitate was filtered off, washed with diethyl ether and dried in air. Hydroxylammonium 1-oxido-5H-tetrazolate (6) was obtained as a yellowish powder in good yield (546 mg, 4.59 mmol, 79%). Crystals suitable for single crystal X-ray measurements were obtained by recrystallization from water.

1 H NMR (DMSO-d6, 25°C): \(\delta = 8.51\) ppm (s, 1H, CH); 13C NMR (DMSO-d6, 25°C): \(\delta = 135.0\) ppm (N4-C); IR (ATR, cm\(^{-1}\)): \(\nu = 3160\) (m), 2889 (s), 2791 (s), 1864 (w), 1643 (w), 1597 (w), 1468 (s), 1438 (w), 1371 (w), 1296 (s), 1234 (s), 1198 (w), 1158 (m), 1114 (w), 1065 (w), 982 (w), 824 (m), 738 (m), 715 (w), 670 (m), 529 (s), 481 (vs); DTA (5°C min\(^{-1}\)): 176°C (\(T_{\text{onset}}\)); elemental analysis calcld [%] for CHN: 103.09; C 11.65, H 4.89, N 67.94; found: C 11.26, H 4.89, N 68.58; BAM drophammer: > 40 J, BAM friction tester: > 360 N, ESD: > 1500 mJ.

Potassium 1-oxido-5H-tetrazolate (3): Compound 5 (500 mg, 4.85 mmol) was dissolved in water (10 mL) and potassium carbonate (670 mg, 4.85 mmol) was added. The solvent was completely dried off in air, and the solid obtained was extracted with hot ethanol and filtered. After recrystallization, potassium 1-oxido-5H-tetrazolate (3) was filtered off and obtained as a yellow powder in good yield (518 mg, 4.17 mmol, 86%). Crystals suitable for single crystal X-ray measurements were obtained by recrystallization from water.

Hydroxylammonium 1-oxido-5H-tetrazolate (6): Compound 1 (500 mg, 5.81 mmol) was dissolved in ethanol (10 mL) and aqueous hydroxylamine solution (50%, 479 mg, 7.20 mmol) was added. After stirring for 5 minutes at 50°C, the precipitate was filtered off, washed with diethyl ether and dried in air. Hydroxylammonium 1-oxido-5H-tetrazolate (6) was obtained as a yellowish powder in good yield (546 mg, 4.59 mmol, 79%). Crystals suitable for single crystal X-ray measurements were obtained by recrystallization from water.
Trisodium bis(1-oxidotetrazol-5-yl)triazene hexahydrate (10): Compound 10 was obtained as yellow-brown needles in moderate yield (283 mg, 0.73 mmol, 59%).

**13C NMR (D₂O, 25 °C): δ = 153.1 ppm; IR (ATR, cm⁻¹): ν = 3334 (m), 1664 (m), 1639 (m), 1518 (m), 1497 (m), 1444 (m), 1426 (m), 1357 (s), 1302 (s), 1256 (s), 1242 (s), 1210 (s), 1168 (m), 1147 (m), 1114 (m), 955 (m), 817 (m), 753 (m), 735 (m), 653 (m), 645 (m), 582 (s), 561 (vs), 561 (vs), 512 (vs), 491 (vs), 412 (s); DTA (S°C min⁻¹): 338 °C (Tm); elemental analysis calcd [%] for C₇H₃N₆O₄ (394.25): C 44.03, H 2.83, N 40.00; found: C 44.30, H 2.70, N 40.35; "BAM" friction tester: > 40 J; "BAM" friction tester: > 360 N; ESD: > 1500 mJ.

**Tripotassium bis(1-oxidotetrazol-5-yl)triazene trihydrate (11):** Compound 11 was obtained as yellow needles in moderate yield (248 mg, 0.65 mmol, 53%).

**13C NMR (D₂O, 25 °C): δ = 153.2 ppm; IR (ATR, cm⁻¹): ν = 3489 (m), 3478 (m), 3262 (m), 3230 (m), 3084 (m), 1688 (w), 1654 (w), 1521 (m), 1505 (s), 1444 (m), 1419 (m), 1320 (vs), 1254 (s), 1238 (s), 1224 (s), 1213 (s), 1159 (m), 1134 (m), 1023 (w), 999 (w), 952 (w), 808 (s), 747 (m), 734 (s), 716 (m), 678 (m), 620 (s), 561 (s), 480 (m), 458 (s); DTA (S°C min⁻¹): 292 °C (Tm); elemental analysis calcd [%] for C₅H₃N₅O₆ (348.44): C 46.48, H 3.48, N 40.01; found: C 46.32, H 3.46, N 40.03; "BAM" friction tester: > 40 J; "BAM" friction tester: > 360 N; ESD: > 1500 mJ.

**Trituridium bis(1-oxidotetrazol-5-yl)triazene trihydride (12):** Compound 12 was obtained as yellow-brown needles in moderate yield (392 mg, 0.75 mmol, 61%).

**13C NMR (D₂O, 25 °C): δ = 153.2 ppm; IR (ATR, cm⁻¹): ν = 3486 (m), 3158 (s), 2159 (w), 1668 (w), 1562 (w), 1516 (m), 1498 (s), 1482 (m), 1409 (m), 1309 (vs), 1249 (s), 1227 (vs), 1208 (s), 1163 (m), 1146 (m), 1027 (m), 1002 (w), 952 (w), 811 (s), 744 (s), 733 (s), 675 (m), 667 (m), 624 (s), 595 (s), 572 (s), 518 (s), 501 (s), 492 (s), 435 (m); DTA (S°C min⁻¹): 292 °C (Tm); elemental analysis calcd [%] for C₄H₃NiNO₄Rb (520.55): C 4.61, H 1.16, N 29.60; found: C 4.75, H 1.46, N 29.53; "BAM" friction tester: > 40 J; "BAM" friction tester: 288 N; ESD: > 750 mJ.

**Triguaniudium bis(1-oxidotetrazol-5-yl)triazene (13):** Compound 13 was obtained as yellow plates in good yield (328 mg, 0.84 mmol, 68%).

**13C NMR (D₂O, 25 °C): δ = 157.9, 153.0 ppm; IR (ATR, cm⁻¹): ν = 3046 (vw), 3349 (vw), 3404 (w), 2815 (w), 1644 (w), 1519 (wv), 1490 (w), 1434 (wv), 1412 (m), 1340 (wv), 1299 (w), 1242 (w), 1229 (w), 1213 (w), 1158 (w), 1140 (w), 1121 (w), 999 (wv), 954 (wv), 880 (wv), 812 (wv), 771 (w), 738 (w), 721 (w), 680 (w), 654 (w), 589 (w), 554 (w), 526 (w), 504 (w), 491 (w), 430 (w), 405 (w); DTA (S°C min⁻¹): 222 °C (Tm); elemental analysis calcd [%] for C₃H₃Ni₂O₆ (390.24): C 15.39, H 4.65, N 70.31; "BAM" friction tester: > 40 J; "BAM" friction tester: > 360 N; ESD: > 1500 mJ.

**Tri(hydroxylammonium) bis(1-oxidotetrazol-5-yl)triazene (14):** Compound 14 was obtained as a pale yellow solid in moderate yield (228 mg, 0.73 mmol, 59%).

IR (ATR, cm⁻¹): ν = 3597 (m), 3511 (w), 3157 (w), 3059 (m), 3048 (m), 2858 (m), 2724 (s), 2445 (s), 1606 (s), 1558 (m), 1519 (m), 1497 (m), 1472 (s), 1460 (s), 1440 (s), 1415 (s), 1338 (w), 1286 (m), 1263 (s), 1245 (s), 1234 (s), 1199 (vs), 1146 (s), 1126 (s), 1029 (m), 1016 (m), 1004 (m), 991 (m), 933 (s), 886 (m), 810 (s), 742 (m), 727 (m), 710 (m), 692 (m), 668 (m), 645 (s), 576 (m), 483 (m), 445 (m), 426 (m), 403 (s); DTA (S°C min⁻¹): 148 °C (Tm); elemental analysis calcd [%] for C₄H₃N₂O₆ (312.21): C 6.39, H 3.87, N 62.81; found: C 6.05, H 3.64, N 61.28; "BAM" friction tester: 128 N; ESD: > 750 mJ.
Ammonium copper(II) bis[1-oxidotetrazol-5-yl]triazeneide (15):
Aqueous sodium nitrite (85.3 mg, 1.24 mmol, 5 mL) was added to a solution of 5-amino-1-hydroxytetrazole (250 mg, 2.47 mmol) in hydrochloric acid (2 mL, 5 mL) and cooled to 0–5 °C. After stirring for 30 minutes, the pH of the solution was adjusted to pH ≥ 10 by adding aqueous sodium hydroxide solution (32%, 5 mL) and stirred at 35°C for another 30 minutes. Copper sulfate pentahydrate (926.4 mg, 3.71 mmol) dissolved in water (5 mL) was added to the reaction solution, and after stirring for 5 minutes, the precipitate was filtered off and washed with water. Recrystallization from aqueous ammonia resulted in compound 15 as green crystalline plates in moderate yield (205 mg, 0.52 mmol, 42%).

IR (ATR, cm⁻¹): ν = 3323 (m), 3259 (m), 3176 (m), 1609 (m), 1536 (m), 1466 (m), 1433 (w), 1374 (vs), 1319 (s), 1298 (s), 1250 (vs), 1237 (vs), 1219 (vs), 1122 (m), 1052 (m), 1005 (m), 976 (m), 833 (m), 750 (s), 679 (s), 574 (s), 536 (s), 527 (s), 499 (s), 476 (s), 457 (s), 445 (s), 433 (s); DTA (5°C·min⁻¹): 212°C (T_mel); elemental analysis calcld [%] for C₁₅H₂₄CuN₁₅O₃: C 6.95, H 2.92, N 48.62; found: C 6.88, H 2.92, N 48.62; BAM drop hammer: 11 J; BAM friction tester: 288 N; ESD: 380 mJ.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: tetrazoles · explosives · triazenes · diazotation · dediazonization

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