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PAPER

5,5′-Azoxytetrazolates – a new nitrogen-rich dianion and its comparison to 5,5′-azotetrazolate†

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A modification of the synthesis of sodium 5,5′ azotetrazolate pentahydrate, described by Thiele in 1898, yields the unknown and unexpected corresponding 5N oxido derivative sodium 5,5′ azoxybistetrazolate pentahydrate ($Na_2zTO\cdot 5H_2O$, **1**). Purification was achieved by recrystallization based on the better solubility of $Na_2zTO\cdot 5H_2O$ in water. Different nitrogen rich salts, such as the diammonium (**3**), the dihydroxylammonium (**4**), the bis diaminoguanidinium (**5**), the bis triaminoguanidinium (**6**) and the diaminouronium salt (**7**), have been prepared using metathesis reactions starting from barium 5,5′ azoxybistetrazolate pentahydrate (**2**) and ammonium, hydroxylammonium, diaminoguanidinium or diaminouronium sulfate and triaminoguanidinium chloride, respectively. The nitrogen rich azoxy derivatives **3** **7** were characterized using NMR, IR and Raman spectroscopy, mass spectrometry and elemental analysis. Additionally the solid state structures of **3**, **4**, **5** and **7** were determined by single crystal X ray diffraction. The heats of formation of **3** and **4** and their corresponding azo tetrazolate derivatives were calculated by the atomization method based on CBS 4M enthalpies. With these values and the crystal densities, several detonation parameters such as the detonation velocity, detonation pressure and specific impulse were calculated (EXPLO5) and compared. The sensitivities towards shock (BAM drophammer), friction (BAM friction tester) and electrostatic discharge of the described compounds were determined.

Introduction

The azo coupling of nitrogen rich heterocycles such as 5 amino tetrazole under alkaline conditions leads to sodium 5,5′ azotetrazolate.[1] In the literature, a broad variety of metal and non metal 5,5′ azotetrazolates has been described including their structural determination by X ray single crystal diffraction. At the moment more than 68 entries for azotetrazolates can be found only in the CCDC database. More than 200 references are listed in the SCIFINDER database containing the azotetrazolate dianion (zT^{2-}). 123 years after their discovery by Thiele,[1] salts of 5,5′ azotetrazole have found various applications mainly in the energetic materials sector including, due to their high nitrogen content, the use as gas generating agents in propellant systems. For example, the bis(triaminoguanidinium) salt[2] (Fig. 1) finds application as a nitrogen rich additive in the NILE propellant (Navy Insensitive Low Erosion Propellant).[3]

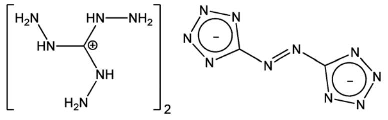

Fig. 1 Bis(triaminoguanidinium) 5,5′ azotetrazolate (TAG_2zT), a nitrogen rich energetic material of great interest.

Tetraamine copper 5,5′ azobis(tetrazolate) dihydrate was recently described as being a “green” additive in solid rockets as a low smoke propellants ingredient.[4] Even several lanthanoid complexes have been published by Austrian coworkers in 2009.[5] They claimed luminescent or nonlinear optic properties of potential interest. Very recently we also described the silver amine azotetrazolate complex as a new primary explosive.[6] Unfortunately, 5,5′ azotetrazolates are not stable under mineral acidic conditions since neutral 5,5′ azotetrazole decomposes into 5 hydrazinotetrazol, dinitrogen and formic acid.[7]

By a small variation in the synthesis of 5,5′ azotetrazole, which is a change of the order of mixing the reagents, sodium 5,5′ azoxybistetrazolate pentahydrate could be isolated. N oxides are getting more and more popular in the development of new energetic materials.[8] The N oxide formation at one of the azo bridge nitrogen atoms changes the properties of the isolated species notably. Not only that the crystal density, which is a very important parameter when calculating the detonation

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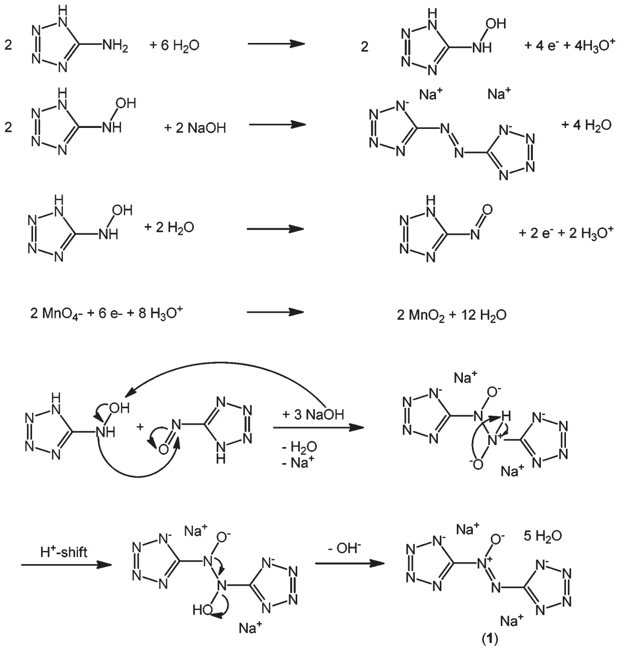
performance of a new material, is dramatically affected by further possibilities to form hydrogen bonds in the solid state, but also the increased oxygen content makes the materials suitable alternatives to 5,5′ azotetrazolates when residue free combustion of the compound is desired. Further we expect a change in the melting and decomposition temperatures of these materials. In the following, the synthesis and characterization of five nitrogen rich salts including the diammonium (**3**), the dihydroxylammonium (**4**), the bis diaminoguanidinium (**5**), the bis triaminoguanidinium (**6**) and the bis diaminouronium (**7**) salt are described, whereas the main attention is directed to the comparison of their physicochemical properties to those of selected respective 5,5′ azotetrazolates.

Results and discussion

Synthesis

Sodium 5,5′ azotetrazolate pentahydrate, as described by Thiele in 1898,[1] can be easily prepared in a one step reaction starting from 5 aminotetrazole *via* oxidation with potassium permanganate. By using the same reagents, but reacting them in a different order, sodium 5,5′ azoxybistetrazolate pentahydrate ($Na_2zTO \cdot 5H_2O$) could be isolated in 16% yield (not optimized protocol). The difference compared to the synthesis of sodium 5,5′ azotetrazolate is that 5 aminotetrazole is added to the oxidizing agent potassium permanganate. A proposed mechanism of the formation of 5,5′ azoxybistetrazolate in comparison to the formation of 5,5′ azotetrazolate is depicted in Scheme 1. A similar process was already observed for the formation of azoxybenzene from solutions of phenyl hydroxylamine upon air oxidation to nitrosobenzene and following condensation with phenylhydroxylamine to form azoxybenzene.[9] Here, 5 aminotetrazole is oxidized to 5 hydroxylaminotetrazole and partially further oxidized to 5 nitrosotetrazole, which together with 5 hydroxylaminotetrazole condensates to 5,5′ azoxy bistetrazolate.



Scheme 1 Mechanism for the formation of 5,5′ azotetrazolate and **1**.

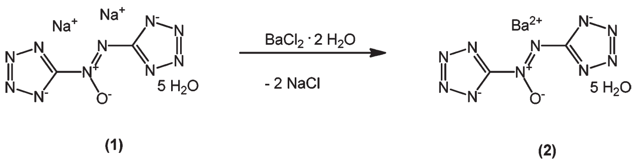
The excess of potassium permanganate firstly ensures the oxidation of 5 hydroxylaminotetrazole to 5 nitrosotetrazole and makes it impossible for the hydroxylaminotetrazole to self condensate, which would result in the formation of 5,5′ azotetrazolate. This is the case if the oxidizing agent potassium permanganate is added to an excess of 5 aminotetrazole under alkaline conditions as described by Thiele.[1] In a further study we tested the influence of the addition of sodium hydroxide to the reaction mixture. For the formation of the azoxy derivative **1** it is only of minor importance whether sodium hydroxide is added at the beginning of the reaction, which supposedly should facilitate the formation of the redox products 5 hydroxylaminotetrazole and 5 nitrosotetrazole, or towards the end of the reaction, where it catalyses the condensation reaction as shown in Scheme 1, indicated by only a small difference in the yields of both synthetic protocols. Instead of 16% yield, we observed 14% yield, when sodium hydroxide is added stoichiometrically at the beginning of the reaction. Therefore, only the protocol, in which sodium hydroxide is added towards the end of the reaction, is described in the experimental part.

For the transformation into the nitrogen rich 5,5′ azoxybistetrazolates, metathesis reactions using the sodium or the barium salt were utilized. The poorly soluble barium salt can be prepared by reacting the sodium salt with 1 equiv. of barium chloride. The barium salt **2** precipitates readily from the aqueous solution and can be filtered off (Scheme 2).

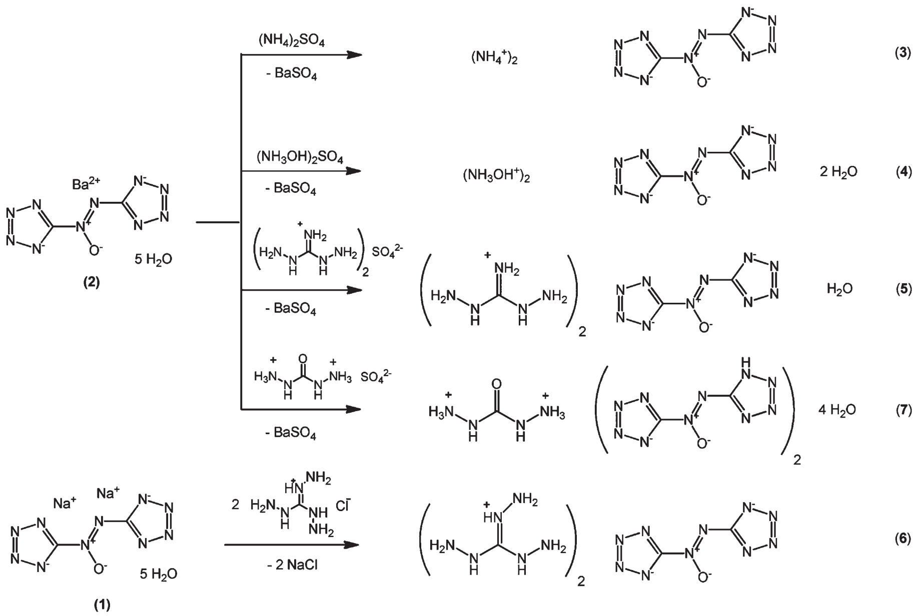
The barium salt **2** was further reacted with the respective nitrogen rich sulfates, which are ammonium sulfate, hydroxylammonium sulfate, diaminoguanidinium sulfate and diaminouronium sulfate. The triaminoguanidinium salt was prepared starting from the sodium salt using triaminoguanidinium chloride.

Except from the triaminoguanidinium salt **6**, single crystals suitable for X ray diffraction of all the remaining compounds **3** **5** and **7** were obtained after recrystallization from either water or an ethanol water mixture. The analytical data in the Experimental section of compound **7** were taken from the compound as isolated from the synthesis without recrystallization, namely bis diaminouronium 5,5′ azoxybistetrazolate (**7a**). Recrystallization from EtOH H_2O however afforded a compound with 1 equiv. of double protonated diaminourea, 2 equiv. of monoprotonated 5,5′ azoxybistetrazolate and four molecules of water per molecular unit, as shown in Scheme 3.

The sulfates, which were used for the metathesis reactions, were obtained from commercial sources (ammonium sulfate, hydroxylammonium sulfate) or prepared as follows. Diaminoguanidinium sulfate was obtained after ion exchange from commercially available diaminoguanidinium chloride. Triaminoguanidinium chloride was prepared from commercially available



Scheme 2 Formation of barium azoxy 5,5′ bistetrazolate (**2**).



Scheme 3 Metathesis reactions leading to the nitrogen rich salts **3** **7**.

aminoguanidinium bicarbonate after acidification with hydrochloric acid to obtain aminoguanidinium chloride and following a hydrazinolysis reaction with hydrazine hydrate in dioxane. Diaminouronium sulfate was obtained after combining solutions of diaminourea (=carbonyldihydrazide) and 1 mol L^{-1} sulfuric acid.

Behavior in acidic media

The chemical stability of the 5,5′ azoxybistetrazolate anion in acidic media compared to the stability of 5,5′ azotetrazolate was tested in 4 experiments by treating both disodium salts with either 0.5 or 1.0 equiv. of 0.01 molar hydrochloric acid on a very small scale (0.33 mmol) after dissolving the salts in 3 mL of water. All four solutions showed gas evolution after a short time, whereas the two solutions containing 5,5′ azotetrazolate showed enhanced gas evolution and also turned red after one day. The two experiments with 5,5′ azoxybistetrazolate stayed yellow even after several days. However a difference between the experiments using 0.5 and 1.0 equiv. of acid could be observed. The solutions using 1.0 equiv. discolored to some extent due to their faster decomposition as compared to the experiments using 0.5 equiv. of acid. The higher stability of the 5,5′ azoxybistetrazolate anion compared to 5,5′ azotetrazolate towards acidic media was already assumed after the solution of the crystal structure of monoprotonated 5,5′ azoxybistetrazolate **7**. To date, no example of a monoprotonated 5,5′ azotetrazolate has been described in the literature.

Single crystal X-ray structure analysis

Compounds **1** **5**, as well as **7** were investigated by low temperature single crystal X ray diffraction. Selected data and parameters of the X ray determinations are given in the ESI (Table S1†). Cif files for the structures have been deposited with the Cambridge Crystallographic Data Centre.[10]

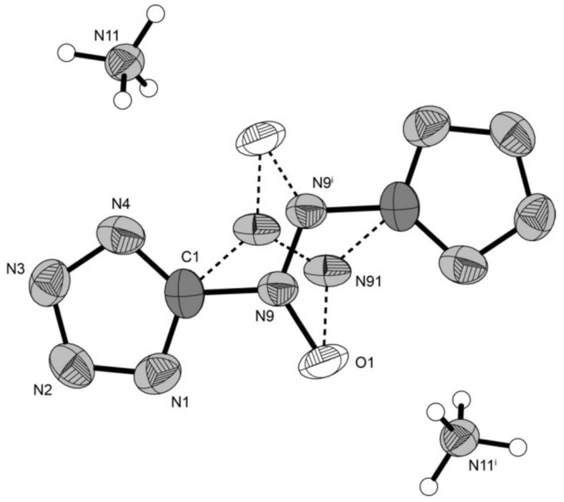


Fig. 2 Molecular unit of diammonium 5,5′ azoxybistetrazolate (**3**). Ellipsoids of non hydrogen atoms are drawn at the 50% probability level. Dashed bonds show the crystallographic disorder of the azoxy group. Symmetry code: (i) 1 *x*, *y*, 1 *z*.

The molecular structure of diammonium 5,5′ azoxybistetrazolate (**3**) revealing the disordered azoxy moiety is shown in Fig. 2. This kind of disorder can be found in most of our investigated azoxy structures. In comparison to ammonium 5,5′ azotetrazolate ($(NH_4)_2zT$)[11] with a density of 1.562 g cm^{-3} (both crystallize in the triclinic space group *P*1) **3** shows a slightly higher density of 1.592 g cm^{-3}. The bond length and angles of the tetrazolate rings are between typical C N/N N single and C=N/N=N double bonds[12] due to the aromaticity. The azoxybistetrazolate dianion is shaped (nearly) planar. The diazene bond length N9 $N9^i$ is 1.27(1) Å which is similar in $(NH_4)_2zT$

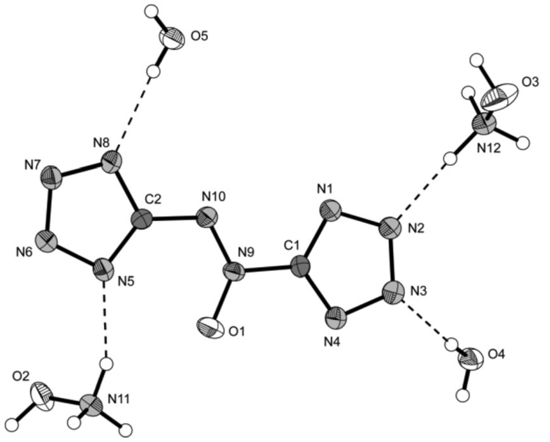


Fig. 3 Molecular unit of dihydroxylammonium 5,5′ azoxybistetrazolate dihydrate (**4**). Ellipsoids of non hydrogen atoms are drawn at the 50% probability level. Selected bond lengths (Å): N11 O2 1.410(2), N12 O3 1.408(3), N10 N9 1.273(2), N10 C2 1.396(3), N4 C1 1.318(2), N4 N3 1.341(2), N7 N6 1.316(2), N7 N8 1.334(2), C1 N1 1.320(2), C1 N9 1.440(3), N9 O1 1.253(2), N8 C2 1.341(3), N5 C2 1.336(3), N5 N6 1.346(2), N1 N2 1.340(2), N3 N2 1.324(2); selected bond angles (°): N9 N10 C2 116.93(17), C1 N4 N3 103.50(16), N6 N7 N8 109.52(16), N4 C1 N1 114.19(18), N4 C1 N9 122.30(18), N1 C1 N9 123.50(18), O1 N9 N10 128.99(18), O1 N9 C1 116.56(16), N10 N9 C1 114.44(16), N7 N8 C2 104.37(16), C2 N5 N6 103.51(17), C1 N1 N2 103 54(16), N2 N3 N4 109.42(16), N3 N2 N1 109.35(16), N7 N6 N5 110.15(16), N5 C2 N8 112.44(18), N5 C2 N10 130.69(19), N8 C2 N10 116.87(18).

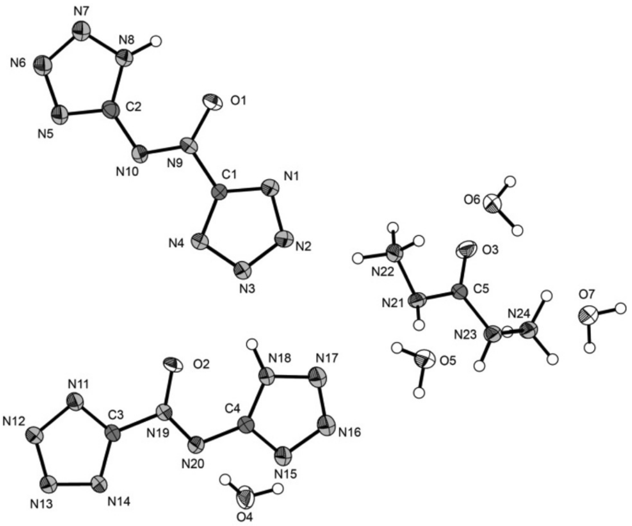


Fig. 4 Molecular unit of diaminouronium bis(5,5′ azoxybistetrazolate) tetrahydrate (**7**). Ellipsoids of non hydrogen atoms are drawn at the 50% probability level. Selected bond lengths (Å): N21 C5 1.367(3), N23 C5 1.364(3), O3 C5 1.219(3), N21 N22 1.420(3), N23 N24 1.430(3); selected bond angles (°): O3 C5 N23 123.3(2), O3 C5 N21 122.7(2), N22 N21 C5 113.59(18), N24 N23 C5 113.58(18).

(1.36(1) Å) and slightly longer than a typical N═N double bond (1.20 Å). The N O bond length is 1.316(8) Å which is between a typical N O single (1.45 Å) and N═O double (1.17 Å) bond. In the structure of **3** there is no difference between the two C1 N9 bonds due to the symmetry centre caused by the disorder.

In accordance with the structure of hydroxylammonium 5,5′ azotetrazolate dihydrate[13] (monoclinic, $C2/c$, $Z = 4$, $\rho = 1.612$ g cm^{-3}), the corresponding N oxide **4**, shown in Fig. 3, crystallizes also under inclusion of two molecules of crystal water in the monoclinic space group $P2_1/c$. As mentioned before, N oxides have been described[14] as promising energetic materials because of increasing densities and thermal stabilities. However, comparison of the hydroxylammonium structures shows a lower density for the N oxide (**4**: 1.596 g cm^{-3}) but an increase in thermal stability ($(Hx)_2zT$: 130 °C *vs.* **4**: 175 °C). The molecular structures of the dianions in **4** are similar to those observed for **3**. However, the dianions are not disordered in this structure. Therefore the influence of the N bonded oxygen atom can be seen by the elongation (~0.05 Å) of the C1 N9 bond of 1.440(3) Å in comparison to the distance of C2 N10 (1.396(3) Å). Again the diazo distance N9═N10 is 1.273(2) Å.

Recrystallization of the residue of the 1 : 1 reaction of barium 5,5′ azoxybistetrazolate and diaminouronium sulfate from 40% hydrofluoric acid yielded the monoprotonated 5,5′ azoxybistetrazolate with a twice positively charged diaminouronium cation and inclusion of four crystal water molecules (Fig. 4). It is the first example of a structurally determined monoprotonated derivative of 5,5′ azotetrazolate, whose existence can be rationalized by the formation of the intramolecular hydrogen bridges (graph set S1,1(6)) N8 H8···O1 (0.92(3), 2.17(3), 2.604(3) Å, 107.8(19)°) and N18 H18···O2 (0.92(3), 2.18(3), 2.562(2) Å, 104(2)°). The compound crystallizes in the monoclinic space group $P2_1/c$ with four cation/anion pairs in the unit cell and a calculated density of 1.650 g cm^{-3} which is the highest one of the metal free compounds investigated in this work. The bond lengths (Table S1†) of the ring atoms are not influenced by the observed protonation. However, the diazene distances N9(19)═N10(20) are slightly elongated in comparison to the structures discussed previously. The diaminouronium cation is not planar showing a torsion angle N22 N21 N23 24 of ~59.1° (Fig. 4).

The structure of disodium 5,5′ azotetrazolate ($Na_2zT{\cdot}5H_2O$) pentahydrate has been described in the literature twice.[7,15] The structure of the sodium salt **1** is quite similar also crystallizing with inclusion of five molecules of crystal water in the triclinic space group $P1$. Its density of 1.720 g cm^{-3} is slightly higher than in $Na_2zT{\cdot}5H_2O$ (1.684 g cm^{-3}). The Na1 cations are distortedly octahedrally coordinated. Sodium 1 is surrounded by the five water oxygen atoms O2, O3, O4, O5^{i}, O4^{ii} and nitrogen atom N3 with distances between 2.38 and 2.46 Å. Sodium 2 shows a larger coordination sphere with longer distances. It is surrounded by the atoms O6, O5 and O6^{i} with similar distances of ~2.42 Å and by the atoms N10, O1A, O3^{i}, O1A^{i} and N4^{i} (~2.58 2.7 Å) in larger distances. Symmetry codes: (i) $-x$, $2 - y$, $1 - z$; (ii) $1 - x$, $2 - y$, $-z$. Due to the described coordination alternating azoxybistetrazolate layers and water layers are formed (Fig. 5 and 6).

NMR spectroscopy

^{1}H and ^{13}C NMR spectroscopy was applied to all of the investigated compounds **1** **7**. Additionally a $^{15}N\{^{1}H\}$ NMR spectrum was recorded of the diammonium salt of 5,5′ azoxy tetrazole (**3**) and for a comparison, a second one of the respective literature known non oxide compound diammonium 5,5′ azotetrazolate.

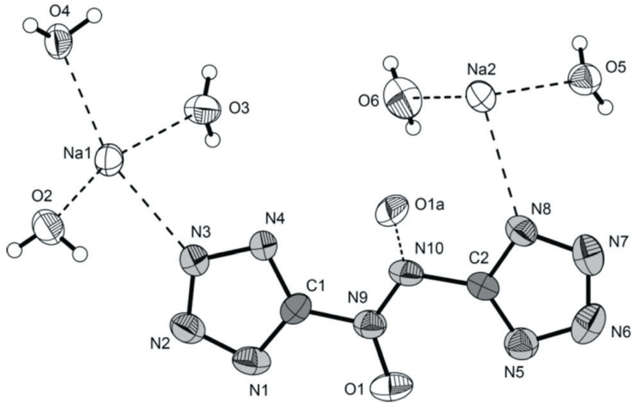


Fig. 5 Molecular unit of disodium 5,5′ azoxybistetrazolate pentahydrate (**1**). Ellipsoids of non hydrogen atoms are drawn at the 50% probability level. Selected bond lengths (Å): Na1 O4 2.389(2), Na1 O2 2.393(2), Na1 O3 2.468(2), Na1 N3 2.457(2), Na2 O5 2.417(2), Na2 O6 2.420(3), Na2 N8 2.613(2).

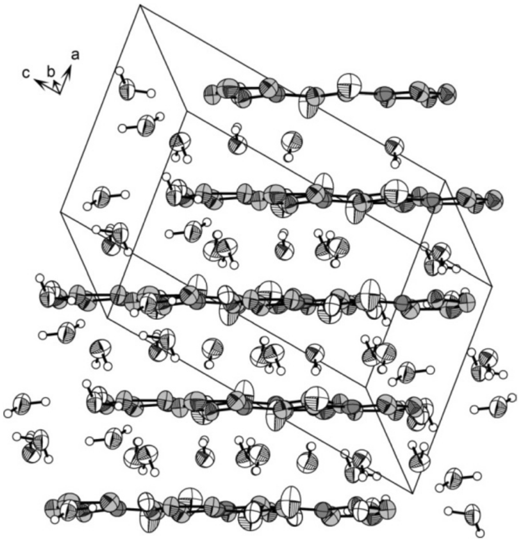


Fig. 6 View on the layer packing in the structure of **1**.

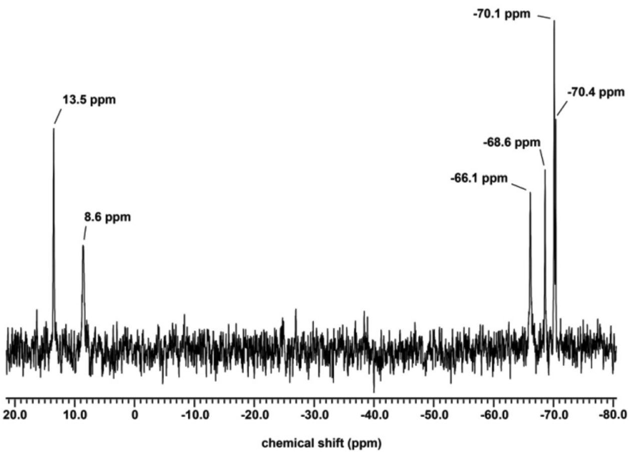


Fig. 7 $^{15}\mathrm{N}\{^{1}\mathrm{H}\}$ NMR spectrum of diammonium 5,5′ azoxybistetrazolate (**3**) in the region between 20 and 80 ppm revealing the six signals observed for the 5,5′ azoxybistetrazolate dianion.

The proton NMR spectra of the metal salts **1** and **2** reveal only crystal water signals at 3.40 ppm (**1**) and 3.36 ppm (**2**), which is also true for the hydrated compound **5** (3.40 ppm). The protons of the ammonium cation of **3** appear as a broad signal at 3.70 ppm, whereas the signal of the protons of the hydroxyl ammonium cation in **4** is downfield shifted to 8.61 ppm (s, br). The aminated guanidinium derivatives **5** and **6** show proton signals at 8.02 (**5**, NH) and 8.60 ppm (**6**, NH) in their spectra and additional upfield shifted signals at 4.60 (**5**) and 4.51 ppm (**6**), which can be assigned to the C and N amino groups of their cations. A similar pattern is observed for the diaminouronium salt **7** with signals at 7.82 ppm (NH) and 6.82 ppm (NNH_3^+, NNH_2).

In the carbon NMR spectra of **1** **7** two signals at chemical shifts of 168.2 168.5 and 162.5 164.3 ppm can be observed, whereas a final assignment to the two chemically inequivalent carbon atoms cannot be made without further investigations. Compared to the carbon atom shift of the signal of 5,5′ azotetrazolates (around 173.2 ppm[16]), the signals of the azoxy derivatives are somewhat shifted upfield indicating a lower shielding of the carbon atom cores.

The $^{15}\mathrm{N}\{^{1}\mathrm{H}\}$ NMR spectrum of diammonium 5,5′ azotetrazolate reveals, due to its symmetry (D_{2h}) and the possible free rotation around the N_{azo} $C_{tetrazole}$ bond, a set of 3 signals, which can be assigned to the anion, and one additional signal for the ammonium cation. The assignments were carried out after comparison to literature known values of the same anion.[16] The signal of the ammonium cation is visible in the upfield region of the spectrum as a singlet at −358.5 ppm. Two signals are observed for both tetrazole rings at 12.8 ppm (N_β) and −66.3 ppm (N_α). The azo bridge nitrogen atoms reveal a signal at 106.6 ppm. The addition of an oxygen atom to the azo bridge changes the symmetry of the anion to lower symmetry (C_s) resulting in a larger number of observed signals in its $^{15}\mathrm{N}\{^{1}\mathrm{H}\}$ NMR spectrum. Here 6 signals of the anion and one additional signal of the cation are observed. A partial assignment was undertaken according to a GIAO NMR calculation with Gaussian09.[36] Two signals in the downfield region at 13.5 and 8.6 ppm can be assigned to the N_β atoms of both tetrazole rings. The exact assignment of the remaining four signals to the two azoxy bridge nitrogen atoms, as well as the two N_α atoms of the tetrazole rings is comparatively difficult since all signals are observed within a range of 4.3 ppm, whereas two of them differ only by 0.3 ppm (−66.1, −68.6, −70.1 and −70.4 ppm). The remaining signal in the upfield region of the spectrum at −358.8 ppm can again clearly be assigned to the ammonium cation. Fig. 7 shows the $^{15}\mathrm{N}\{^{1}\mathrm{H}\}$ NMR spectrum of the anion of **3**, the signals of which are observed in the region between 20 and −80 ppm.

If the $^{15}\mathrm{N}\{^{1}\mathrm{H}\}$ NMR spectra of both above discussed compounds are compared, it can be stated that N oxidation at the azo bridge of the anion mainly affects the chemical shifts of the nitrogen atoms in the azo bridge itself. The signals are strongly shifted upfield from 106.6 ppm for the azo bridge N atoms to signals in the vicinity of −68 ppm for the azoxy bridge. Neither the N_α (12.8 ppm for the azo compound *vs.* 13.5/8.6 ppm for **3**) nor the N_β (−66.3 ppm for the azo compound *vs.* signals at −66.1 to −70.4 ppm for **3**) atoms of the tetrazole rings are shifted significantly to higher or lower field.

Vibrational spectroscopy

Also Raman and IR spectroscopy were applied for the identification of **1**–**8**. Generally, the crystal water containing compounds **1**, **2**, **4** and **5** show absorptions in the region between 3030 and 3422 cm^{-1} in their IR spectra due to O–H valence vibrations. Additionally, N–H valence vibration absorptions of all nitrogen-rich cation (ammonium, hydroxylammonium, diaminoguanidinium, triaminoguanidinium and diaminouronium) containing compounds **3**–**7** are observed in the region 3171–3388 cm^{-1}.

Further characteristic absorption bands, which are observed for azoxybistetrazolates, are based on the $C_{tetrazole}$–N_{azoxy} valence vibration at 1390–1412 cm^{-1} and the N═N azoxy valence vibration at 1499–1504 cm^{-1}. The guanidinium derived cations in **5** and **6** reveal absorption bands of the C–N stretching vibration at 1685 cm^{-1} (**6**) and 1684/1667 cm^{-1} (**5**). The ammonium salt **3** additionally can be identified by the deformation vibration of its cation visible in a strong absorption band at 1430 cm^{-1}. Although the mentioned absorption bands prove the identity of the synthesized compounds, due to a large number of combination modes, especially in the IR spectra, not all absorption bands could be assigned.

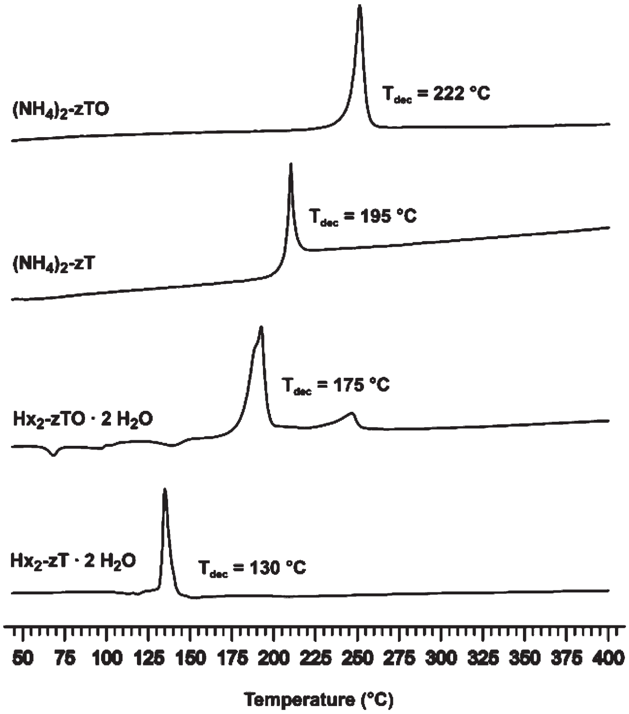


Fig. 8 DSC curves of **3** ($(NH_4)_2$zTO) and **4** (Hx_2zTO) and their corresponding non-oxide dihydroxylammonium 5,5′-azotetrazolate (Hx_2zT) and diammonium 5,5́-azotetrazolate ($(NH_4)_2$zT).

Thermal behavior

Differential scanning calorimetry (DSC) measurements to determine the melt- and decomposition temperatures of **1**–**8** (about 1.5 mg of each energetic material) were performed in covered Al containers with a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mL min^{-1} at a heating rate of 5 °C min^{-1}. The decomposition temperatures are given as onset temperatures and are within a range from 160 °C (**7a**) to 222 °C (**1** and **3**). The sodium salt **1** loses its hydrate water, indicated by an endothermic peak in the DSC trace at 80–130 °C, which is also true for the barium salt **2** at 100–130 °C. However, the barium salt decomposes earlier (188 °C) compared to the sodium salt (222 °C). If comparing the two metal salts to their 5,5′-azotetrazolate analogues, the decomposition temperatures of the 5,5′-azotetrazolates are somewhat higher ($Na_2zT{\cdot}5H_2O$: 248 °C; $BazT{\cdot}5H_2O$: 211 °C[7]). The opposite trend is observed if comparing the ammonium and the hydroxylammonium (Hx^-) salts of both anions. Both ammonium salts crystallize water free with decomposition temperatures of 222 °C for the 5,5′-azoxybistetrazolate (**3**) and only 195 °C for the corresponding 5,5′-azotetrazolate. Both hydroxylammonium salts crystallize as dihydrate and decompose much earlier at 175 °C (**4**) and 130 °C (corresponding 5,5′-azotetrazolate). They lose their crystal water at 60–150 °C (**4**) and 105–125 °C (5,5′-azotetrazolate) respectively. Fig. 8 clearly shows the observed trend of higher decomposition temperatures of the ammonium salts compared to their corresponding hydroxylammonium salts as well as the observed trend of higher decomposition temperatures of the azoxy derivatives **3** and **4** compared to their non-oxide analogs $(NH_4)_2$zT and Hx_2zT, which, astonishingly, is not true for the sodium and the barium salts of these anions as described above. All decomposition temperatures are summarized in Table 3.

Sensitivity testing

For application of new energetic compounds important values for safety, handling and processing are the sensitivity data. The values for friction and impact sensitivity were determined according to BAM (Bundesanstalt für Materialforschung) standard methods described in the NATO STANAG 4487, 4489 and 4490 specifications for energetic materials using a BAM friction tester and a BAM drophammer.[17–24] The sensitivities towards electrical discharge were determined on a small scale electrostatic discharge device.[25]

According to the UN recommendations on the transport of dangerous goods, the sodium salt **1** can be regarded as less sensitive towards impact with a value of 40 J, whereas the barium salt, although being a pentahydrate, is much more sensitive (7 J). The same trend is observed for the friction sensitivity of both salts (**1**: 324 N; **2**: 160 N). The comparatively low sensitivity of the sodium salt can mainly be explained by the formation of the pentahydrate, since contained crystal water usually desensitizes a compound. The remaining nitrogen-rich salts **3**–**7** need to be classified as sensitive (**4**–**7**) or very sensitive (**3**) towards impact, however there are still large differences in their impact sensitivity data. Whereas the dihydroxylammonium salt **4** reveals an impact sensitivity of 30 J, which again can be explained by the formation of a dihydrate, the bis-diaminoguanidinium salt **5** (as its monohydrate) has a value of only 15 J and both the bis-triaminoguanidinium salt **6** and the bis diaminouronium salt **7** are already close to being classified as very sensitive towards impact (**6**: 4 J; **7**: 3.5 J), which is true for the diammonium salt **3** with an impact sensitivity of only 1 J (!). The friction sensitivities of the above discussed compounds **4** **7** are in a range between 120 N for **6** and 324 N for **5**, whereas both kinds of sensitivity data do not seem to be directly related to each other as evidenced by the bis diaminouronium salt **7**, which is rather sensitive towards impact (3.5 J) but on the other hand shows only a moderate value for the friction sensitivity (240 N). The ammonium salt again shows the highest sensitivity amongst the discussed compounds (40 N). The sensitivities towards electrostatic discharge are in a range between 0.2 J (**1**) and 0.50 J (**5**, **7**). Through normal activities, the human body can generate up to 25 mJ of static electricity, which can easily set off the most sensitive explosives. All compounds presented herein have electrostatic sensitivities higher than the one possibly being generated by the human body, allowing safety during handling. Only the value of **6** (90 mJ) is noticeably low, but the non crystallinity of **6** can be a possible reason for this result, since the sensitivity towards electrostatic discharge is also dependent on the grain size of the investigated material.

Heats of formation

The heats of formation of water free **3** and $(NH_4)_2zT$ as well as of **4** and $Hx_2zT{\cdot}2H_2O$ for comparison were calculated with the atomization method (eqn (1)) using CBS 4M enthalpies and summarized in Table 1.[26,27] Heats of formation of the other hydrated compounds and of the triaminoguanidinium salt, of which the density could not be determined by XRD, were neglected. The gas phase enthalpies of formation $\Delta_f H°$ (g, M) were converted into the solid state enthalpies of formation ($\Delta_f H°$ (s, M)) by using the Jenkins' equations for X_2Y salts[28] (for ionic derivatives).

$$\Delta_f H°_{(g,M,298)} = H_{(M,298)} - \sum H°_{(Atoms,298)} + \sum \Delta_f H°_{(Atoms,298)} \quad (1)$$

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to eqn (2) (Table 2).

$$\Delta U_m = \Delta H_m - \Delta n\,RT \quad (2)$$

(Δn being the change of moles of gaseous components).

A more positive heat of formation for the solid state was calculated for $(NH_4)_2zT$ (547 kJ mol^{-1}) (which was expected) in comparison to the N oxide **3** (519 kJ mol^{-1}).

Table 1 Gas phase enthalpies of formation based on CBS 4M calculations

M	Formula	$H_{(M,\ 298)}$[a]/a.u.	$\Delta_f H°$[b] (g, M)/kJ mol^{-1}
zTO^{2-}	$C_2N_{10}O^{2-}$	697.959163	711.2
zT^{2-}	$C_2N_{10}{}^{2-}$	622.850742	769.6
$NH_4{}^+$	$NH_4{}^+$	56.796608	635.8
Hx^+	NH_3OH^+	131.863229	687.2

[a] Electronic enthalpies in Hartree. [b] Calculated gas phase heat of formation of the involved anions and cations.

Detonation parameters

In order to explore the performance of the highly energetic backbone 5,5′ azoxybistetrazolate, several detonation parameters of its diammonium and dihydroxylammonium salts **3** and **4** were calculated with the EXPLO5.05[29] software code and compared to those for diammonium and dihydroxylammonium 5,5′ azotetrazolate (Table 3). In the case of the ammonium salts, which crystallize water free, also the calculated specific impulse under isobaric conditions is discussed. The program EXPLO5 is based on the steady state model of equilibrium detonation and uses Becker Kistiakowsky Wilson's equation of state (BKW E.O.S.) for gaseous detonation products and Cowan Fickett's E.O.S. for solid carbon.[30] The calculation of the equilibrium composition of the detonation products is done by applying the modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the Chapman Jouguet point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated below the equations and X_i being the mole fraction of the i th gaseous product, k_i is the molar covolume of the i th gaseous product:[31]

$$pV/RT = 1 + xe^{\beta x}$$

$x = (\kappa \Sigma X_i k_i)/[V(T + \theta)]^{\alpha}$, $\alpha = 0.5$, $\beta = 0.176$, $\kappa = 14.71$, $\theta = 6620$.

In terms of performance **3** is superior to the corresponding non N oxide $(NH_4)_2zT$. Due to the higher oxygen content a

Table 2 Lattice energies and enthalpies as well as solid state enthalpies and energies of formation ($\Delta_f U°$)

	Formula	M/g mol^{-1}	$\Delta_f H°$[a] (g)/kJ mol^{-1}	V_M[b]/nm^3	U_L[c]/ kJ mol^{-1}	ΔH_L[d]/ kJ mol^{-1}	$\Delta_f H°$[e] (s)/ kJ mol^{-1}	Δn	$\Delta_f U°$[f] (s)/ kJ mol^{-1}
$(NH_4)_2zT$	$C_2H_8N_{12}$	200.2	2041.3	0.213	1482.4	1489.9	551.4	10	576.2
3	$C_2H_8N_{12}O$	216.2	1982.9	0.225	1451.9	1459.3	523.6	10.5	549.6
$(Hx)_2zT{\cdot}2H_2O$	$C_2H_{12}N_{12}O_4$	268.11	1660.9	0.227	1554.9	1567.3	93.6	14	128.3
4	$C_2H_{12}N_{12}O_5$	284.1	1602.5	0.247	1510.5	1522.9	79.5	14.5	115.5

[a] Calculated gas phase heat of formation of the ionic compounds. [b] Molecular volumes calculated from the X ray structures (*V*/*Z*). [c] Lattice energy. [d] Lattice enthalpy. [e] Calculated heat of formation of the ionic compounds in the solid state. [f] Calculated energy of formation of the ionic compounds in the solid state.

Table 3 Energetic properties and detonation parameters of **3**, **4**, $(NH_4)_2zT$ and $Hx_2zT\cdot 2H_2O$

	3	$(NH_4)_2zT$	**4**	$Hx_2zT\cdot 2H_2O$
Formula	$C_2H_8N_{12}O$	$C_2H_8N_{12}$	$C_2H_{12}N_{12}O_5$	$C_2H_{12}N_{12}O_4$
MW [g mol^{-1}]	216.2	200.2	284.1	268.11
IS[a] [J]	1	3	30	25
FS[b] [N]	40	42	160	192
ESD test[c] [J]	0.30	0.035	0.25	0.30
N[d] [%]	77.8	84.0	59.1	62.7
Ω[e] [%]	51.8	63.9	28.2	35.8
$T_{dec.}$[f] [°C]	222	195	175	130
Density[g] [g cm^{-3}]	1.592	1.562	1.596	1.615
$\Delta_f H_m^\circ$[h] [kJ mol^{-1}]	+524	+551	+80	+94
$\Delta_f U^\circ$[i] [kJ kg^{-1}]	+2542	+2878	+406	+478
EXPLO5.05 values				
I_{sp}[j] [s]	215	207	234	218
$\Delta_E U^\circ$[k] [kJ kg^{-1}]	4039	3437	4723	4271
T_E[l] [K]	2935	2565	3309	3020
p_{C-J}[m] [kbar]	240	216	258	254
D[n] [m s^{-1}]	8054	7788	8224	8200
V_0[o] [L kg^{-1}]	831	824	893	892

[a] Impact sensitivity (BAM drophammer, method 1 of 6). [b] Friction sensitivity (BAM friction tester, method 1 of 6). [c] Small scale electrostatic discharge device (OZM). [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C). [g] Estimated from X ray diffraction. [h] Calculated (CBS 4M) heat of formation. [i] Calculated energy of formation. [j] Specific impulse (isobaric combustion with a chamber pressure of 60 bar). [k] Energy of explosion. [l] Explosion temperature. [m] Detonation pressure. [n] Detonation velocity. [o] Volume of detonation products assuming only gaseous products.

higher energy of detonation (4039 kJ mol^{-1}) was computed. Because of its slightly higher density (1.592 g cm^{-3} (**3**) *vs.* 1.562 g cm^{-3} ($(NH_4)_2zT$) also the detonation pressure (240 kbar) and velocity (8054 m s^{-1}) are higher. Basically latter detonation values are greater than those observed for TNT but smaller than that of PETN (pentaerythriol tetranitrate) or RDX (hexogen).[32] In addition, the specific impulse of the pure compounds when used as monopropellants was calculated assuming rocket propellant conditions (isobaric combustion with a chamber pressure of 60 bar). Also the calculated specific impulse of **3** is better than that of $(NH_4)_2zT$. The same trend can be proposed for the hydrazinium and triaminoguanidinium salts whose azotetrazolates showed promise as propellant ingredients (see Introduction).

In the case of the two dihydroxylammonium salts dihydrates **4** and $Hx_2zT\cdot 2H_2O$ (against expectations) we observe a slightly lower density of the azoxy compound. Again the heat of formation is slightly decreased by the introduction of the N oxide. However, the less negative oxygen balance of the azoxy compound (−28.2% *vs.* −35.8%) in combination with its slightly higher gas volume (893 L *vs.* 892 L) compensates for both, the slightly lower density and the lower heat of formation, so that the calculated detonation parameters of both salts are almost equal with 258 (**4**) and 254 kbar for both calculated detonation pressures and 8224 ms^{-1} (**4**) and 8200 ms^{-1} ($Hx_2zT\cdot 2H_2O$) for the detonation velocities. If comparing the explosion energy and the detonation temperature, one notices a stronger influence of the N oxidation on these parameters for **4** and $Hx_2zT\cdot 2H_2O$. Also the calculated specific impulse of **4** (234 s) is higher than that of $Hx_2zT\cdot 2H_2O$ (218 s).

Conclusions

From this combined theoretical and experimental study the following conclusions can be drawn:

Sodium 5,5′ azoxybistetrazolate pentahydrate can be isolated from the oxidation of 5 aminotetrazole with potassium permanganate, when 5 aminotetrazole is added to a stirred solution of the oxidizing agent $KMnO_4$.

A proposed mechanism for the formation of 5,5′ azoxybistetrazolate is formulated *via* the condensation of 5 hydroxylamino tetrazole and 5 nitrosotetrazole.

Bearing a numerous amount of inherently energetic C N and N N bonds, sodium 5,5′ azoxybistetrazolate was subjected to various metathesis reactions leading to the isolation and full characterization, including the X ray single crystal measurements of a variety of nitrogen rich salts of this previously undescribed anion.

Compared to 5,5′ azotetrazolates, 5,5′ azoxybistetrazolates show a comparable or even higher density due to better possibilities to form hydrogen bonds in the solid state.

The calculated (CBS 4M) heats of formation of the partially oxidized N oxides are, however, insignificantly lower compared to the respective 5,5′ azotetrazolates.

The difference in thermal behaviour between 5,5′ azotetrazolates and 5,5′ azoxybistetrazolates is varying from compound to compound. The disodium and barium salt of 5,5′ azoxybistetrazole were found to be less thermally stable than the respective 5,5′ azotetrazolates, whereas the nitrogen rich diammonium and dihydroxylammonium salts are thermally more stable than their respective 5,5′ azotetrazolate counterparts.

If comparing the ammonium salt **3** to $(NH_4)_2zT$, it can be stated that based on its higher density, it reveals improved detonation performance, *i.e.* detonation velocity, detonation pressure, detonation temperature and explosion energy.

Experimental part

General procedures

All reagents and solvents were used as received (Sigma Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting and decomposition points were measured with a Linseis PT10 DSC using a heating rate of 5 °C min^{-1}, which were checked with a Büchi Melting Point B 450 apparatus. ^1H, ^{13}C and ^{15}N NMR spectra were measured with a JEOL Eclipse 400 ECX instrument. All chemical shifts are quoted in ppm relative to TMS (^1H, ^{13}C) and nitromethane (^{15}N). Infrared spectra were measured as KBr pellets on a Perkin Elmer Spektrum One FT IR instrument. Raman spectra were recorded on a Bruker MultiRAM FT Raman fitted with a liquid nitrogen cooled germanium detector and a Nd:YAG laser (λ = 1064 nm). Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. Melting points were determined in capillaries with a Büchi Melting Point B 540 instrument and are uncorrected. Decomposition points were determined by differential scanning calorimetry (DSC) measurements with a Linseis DSC PT10 DSC,[33] calibrated by standard pure indium and zinc using a heating rate of 5 °C min^{-1}. Pycnometric measurements were carried out with a Quantachrome helium gas pycnometer.

Sensitivity data (impact and friction) were performed using a drophammer and friction tester analog to BAM standards (Bundesanstalt für Materialforschung und prüfung).[17–24,34] Electrostatic sensitivities were measured with an OZM small scale electrostatic discharge tester.[35] Quantum chemical calculations were performed with the Gaussian09 software.[36] The crystal structures of **1**, **2** and **3** were measured at −65 °C on a Nonius KappaCCD instrument. XRD of **4**, **5** as well as **7** and **8** was performed on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using Mo Kα radiation (λ = 0.71073 Å). The data collection and reduction was carried out using the CRYSALISPRO software.[37] The structures were solved either with SHELXS 97[38] or SIR 92,[39] refined with SHELXL 97[40] and finally checked using the PLATON[41] software integrated in the WINGX[42] software suite. The absorptions of **4**, **5** as well as **7** and **8** were corrected with a Scale3 Abspack multi scan method.[43]

Sodium 5,5′-azoxybistetrazolate pentahydrate (1). Potassium permanganate (17.1 g, 108 mmol, 1.00 equiv.) was dissolved in water (150 mL) and 5 aminotetrazole (12.4 g, 146 mmol, 1.35 equiv.) was added in small portions at 0 °C. The brown reaction mixture was stirred at 0 °C (1 h), room temperature (1 h) and 50 °C (3 h). Ethanol (30 mL, 514 mmol, 4.76 equiv.) and an aqueous solution of sodium hydroxide (15%, 150 mL, 562 mmol, 5.20 equiv.) were added and the thick, brown slurry was stirred at 90 °C (3 h). The still hot mixture was filtered over diatomaceous earth and washed with boiling water as long as the filtrate was still yellow. The solvent was removed by rotary evaporation and the remaining light yellow solid was extracted with hot ethanol. Ethanol was removed by rotary evaporation and the remaining yellow solid was twice recrystallized from EtOH H_2O. Sodium 5,5′ azoxybistetrazolate pentahydrate (2.80 g, 8.80 mmol, 16%) was obtained as clear, yellow crystals.

DSC (T_{onset}, 5 °C min^{-1}): 222 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3835 (w), 3422 (vs), 1632 (m), 1500 (m), 1473 (vw), 1450 (m), 1396 (m), 1275 (w), 1207 (w), 1160 (w), 1061 (w), 1034 (w), 913 (w), 768 (m), 559 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1532 (7), 1503 (64), 1458 (26), 1448 (100), 1401 (49), 1387 (69), 1373 (70), 1282 (4), 1208 (7), 1164 (4), 1100 (40), 1082 (32), 1063 (69), 1050 (29), 924 (4), 754 (3), 401 (4), 252 (8), 89 (36); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 3.40 (H_2O); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.4 (CN_4), 164.0 (CN_4); *m*/*z* (FAB$^+$): 23.0 [Na$^+$]; *m*/*z* (FAB$^-$): 181.1 [$C_2HN_{10}O^-$]; EA ($C_2H_{10}N_{10}O_6Na_2$, 316.14) calcd: N 44.30, C 7.60, H 3.10; found: N 43.57, C 7.78, H 3.06; impact sensitivity: 40 J; friction sensitivity: 324 N; ESD: 0.2 J (at grain size 500 1000 μm).

Barium 5,5′-azoxybistetrazolate pentahydrate (2). Sodium 5,5′ azoxybistetrazolate pentahydrate (2.80 g, 8.80 mmol, 1.00 equiv.) was dissolved in hot water (8 mL) and a hot solution of barium chloride dihydrate (2.15 g, 8.80 mmol, 1.00 equiv.) was added and shortly heated. The solution was allowed to cool down and the resulting yellow precipitate was filtered, recrystallized from EtOH H_2O and dried to obtain barium azoxy 5,5′ bistetrazolate pentahydrate (3.50 g, 8.60 mmol, 98%).

DSC (T_{onset}, 5 °C min^{-1}): 188 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3414 (vs), 1623 (m), 1504 (s), 1473 (w), 1445 (m), 1394 (s), 1286 (w), 1204 (w), 1168 (w), 1071 (w), 1037 (w), 921 (m); 764 (m), 735 (w), 647 (w), 562 (w), 529 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1506 (66), 1484 (18), 1456 (62), 1395 (100), 1376 (66), 1287 (5), 1206 (3), 1191 (2), 1171 (3), 1099 (47), 1079 (66), 1053 (17), 924 (4), 755 (2), 403 (3), 258 (3); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 3.36 (H_2O); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.4 (CN_4), 163.6 (CN_4); *m*/*z* (FAB$^-$): 181.1 [$C_2HN_{10}O^-$]; EA ($C_2H_{10}BaN_{10}O_6$, 407.49) calcd: N 34.37, C 5.89, H 2.47; found: N 34.30, C 5.91, H 2.51%; impact sensitivity: 7 J; friction sensitivity: 160 N; ESD: 0.60 J (at grain size 500 1000 μm).

Diammonium 5,5′-azoxybistetrazolate (3). Barium 5,5′ azoxy bistetrazolate pentahydrate (3.54 g, 8.69 mmol) was suspended in 100 mL of water and a solution of ammonium sulphate (1.15 g, 8.69 mmol) in 20 mL of water was added. The mixture was heated to reflux for 5 min and further stirred at room temperature overnight. $BaSO_4$ was removed by filtration over diatomaceous earth and the filtrate was concentrated in a rotary evaporator. From the concentrated solution, the diammonium salt crystallized in yellow blocks, which were isolated by filtration, washed with the mother liquor several times and dried in air. Yield: 65% (1.73 g, 5.65 mmol).

DSC (T_{onset}, 5 °C min^{-1}): 222 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3173 (m), 3002 (m), 2856 (m), 1692 (m), 1503 (m), 1430 (vs), 1390 (s), 1368 (m), 1276 (w), 1200 (m), 1185 (m), 1163 (m), 1070 (m), 1035 (w), 914 (m), 782 (s), 755 (m), 746 (m), 731 (m), 655 (w), 519 (m); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1530 (10), 1506 (50), 1490 (26), 1441 (100), 1394 (78), 1382 (56), 1371 (77), 1279 (7), 1203 (4), 1168 (5), 1090 (53), 1075 (95), 1047 (21), 918 (5), 757 (3), 402 (2), 256 (6), 183 (4); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 3.70 (s, br, NH_4^+); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.4 (CN_4), 164.3 (CN_4); *m*/*z* (FAB$^+$): 110.1 [NH_3 + matrix$^+$]; *m*/*z* (FAB$^-$): 181.1 [$C_2HN_{10}O^-$]; EA ($C_2H_8N_{12}O$, 216.16) calcd: N 77.76, C 11.11, H 3.73; found: N 77.35, C 11.69, H 3.53%; impact sensitivity: 1 J; friction sensitivity: 40 N; ESD: 0.30 J (at grain size 100 500 μm).

Dihydroxylammonium 5,5′-azoxybistetrazolate dihydrate (4). Barium 5,5′ azoxybistetrazolate pentahydrate (3.41 g, 8.37 mmol) was dissolved in the smallest possible volume of water (*ca.* 100 mL). A solution of hydroxylammonium sulfate (1.37 g, 8.37 mmol) was added. The instantaneously formed precipitate of $BaSO_4$ was removed after centrifugation of the mixture. The supernatant liquid was evaporated to almost dryness, the residue was again slurried in a little water and the mixture was filtered again to remove the remaining $BaSO_4$. The aqueous filtrate was left for crystallization. Yield: 72% (6.04 mmol, 1.50 g).

DSC (T_{onset}, 5 °C min^{-1}): 175 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3385 (s), 2983 (s), 2739 (vs), 2133 (w), 2090 (w), 1659 (w), 1618 (m), 1535 (m), 1499 (m), 1476 (m), 1454 (m), 1412 (m), 1384 (m), 1292 (w), 1253 (w), 1215 (w), 1194 (w), 1187 (w), 1166 (w), 1104 (w), 1082 (w), 1068 (w), 1050 (w), 1042 (w), 995 (w), 917 (w), 773 (m), 753 (m), 725 (w), 655 (w), 626 (w), 520 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1500 (16), 1477 (10), 1453 (100), 1415 (28), 1380 (38), 1294 (3), 1189 (3), 1168 (4), 1105 (68), 1085 (21), 1069 (12), 1052 (5), 997 (5), 919 (2), 758 (1), 402 (2), 266 (4); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 8.61 (s, br, N*H*, O*H*); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.2 (CN_4), 162.5 (CN_4); *m/z* (FAB^+): 34.0 $[NH_3OH^+]$; *m/z* (FAB^-): 181.0 $[C_2HN_{10}O]^-$; EA ($C_2H_{12}N_{12}O_5$, 284.19) calcd: N 59.14, C 8.45, H 4.26; found: N 57.72, C 8.70, H 3.93%; impact sensitivity: 30 J; friction sensitivity: 160 N; ESD: 0.25 J (at grain size 100 500 µm).

Bis-diaminoguanidinium 5,5′-azoxybistetrazolate monohydrate (5). Barium 5,5′ azoxybistetrazolate pentahydrate (0.445 g, 1.09 mmol, 1.00 equiv.) was dissolved in boiling water and added to, previously dissolved in hot water, diaminoguanidinium sulphate (0.304 g, 1.10 mmol, 1.01 equiv.). The mixture was heated (5 min) and the precipitating barium sulphate was filtered off (diatomaceous earth). The light yellow solution was left to crystallize and diaminoguanidinium azoxy 5,5′ bistetrazolate monohydrate (0.260 g, 0.722 mmol, 66%) was obtained as ochre crystals.

DSC (T_{onset}, 5 °C min^{-1}): 179 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3388 (vs), 3336 (vs), 2257 (vw), 1684 (vs), 1667 (vs), 1504 (m), 1541 (w), 1395 (s), 1274 (w), 1173 (m), 1033 (vw), 974 (m), 915 (w), 770 (m), 751 (w), 742 (w), 655 (w), 538 (m); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3335 (4), 1676 (5), 1639 (3), 1506 (69), 1472 (11), 1450 (16), 1429 (83), 1402 (25), 1368 (78), 1275 (5), 1201 (5), 1179 (9), 1166 (8), 1069 (100), 1038 (19), 930 (12), 767 (3), 664 (2), 549 (9), 396 (5), 376 (5), 282 (3), 252 (6), 122 (52), 95 (47), 83 (39); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 8.02 (s, br, N*H*), 4.60 (s, CNH_2, NNH_2), 3.40 (s, H_2O); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.4 (CN_4), 163.8 (CN_4), 160.3 ($C{=}NH_2$); *m/z* (FAB^+): 90.1 $[CH_8N_5]^+$; *m/z* (FAB^-): 181.1 $[C_2HN_{10}O]^-$; EA ($C_4H_{18}N_{20}O_2$, 378.32) calcd: N 74.05, C 12.70, H 4.80; found: N 73.96, C 13.48, H 4.60%; impact sensitivity: 15 J; friction sensitivity: 324 N; ESD: 0.5 J (at grain size 100 500 µm).

Bis-triaminoguanidinium 5,5′-azoxybistetrazolate (6). Sodium 5,5′ azoxybistetrazolate (0.650 g, 2.06 mmol, 1.00 equiv.) and triaminoguanidinium chloride (0.580 g, 4.13 mmol, 2.00 equiv.) were each dissolved in just enough boiling water, combined and brought to the boil. The crude product precipitated during night and was then filtered and washed with a few drops of ice water and ethanol. Triaminoguanidinium 5,5′ azoxybistetrazolate (0.611 g, 1.57 mmol, 76%) was obtained as light yellow thin needles.

DSC (T_{onset}, 5 °C min^{-1}): 190 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3320 (m), 3211 (s), 3030 (m); 2868 (m), 1685 (s), 1503 (m), 1437 (s), 1394 (s), 1369 (m); 1277 (w), 1201 (w), 1129 (w), 1071 (w), 1035 (w), 952 (w), 915 (w), 763 (w), 608 (w), 519 (w), 401 (w), 336 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3337 (2), 3240 (3), 1681 (2), 1531 (6), 1494 (48), 1474 (18), 1434 (101), 1396 (37), 1371 (42), 1362 (65), 1277 (5), 1197 (10), 1162 (3), 1079 (27), 1063 (16), 1047 (81), 919 (5), 885 (6), 641 (1), 402 (5), 246 (5), 141 (12), 93 (23); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 8.60 (s, N*H*), 4.51 (s, NH_2); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.5 (CN_4), 164.0 (CN_4), 159.6 ($C(NHNH_2)_3{}^+$); *m/z* (FAB^+): 105.1 $[CH_9N_6]^+$; *m/z* (FAB^-): 181.1 $[C_2HN_{10}O]^-$; EA ($C_4H_{18}N_{22}O$, 390.2) calcd: N 78.94, C 12.31, H 4.65; found: N 76.16, C 13.17, H 4.80%; impact sensitivity: 4 J; friction sensitivity: 120 N; ESD: 90 mJ (at grain size 100 500 µm).

Bis-diaminouronium 5,5′-azoxybistetrazolate (7a). Barium 5,5′ azoxybistetrazolate pentahydrate (2.04 g, 5.00 mmol, 1.00 equiv.) and diaminouronium sulphate (0.940 g, 5.00 mmol, 1.00 equiv.) were both dissolved in boiling water (30 mL each) as well. The two solutions were combined and diaminourea (0.433 g, 5.00 mmol, 1.00 equiv.) was added. After gas evolution stopped and the mixture was cooled down, the precipitated barium sulphate was filtered off over diatomaceous earth and the filtrate was left to crystallize under a slight nitrogen stream. Bis diaminouronium 5,5′ azoxybistetrazolate (1.23 g, 3.40 mmol, 68%) was obtained as a light yellow solid. Recrystallization from ethanol water however afforded diaminouronium 5,5′ azoxybistetrazolate tetrahydrate (**7**).

DSC (T_{onset}, 5 °C min^{-1}): 160 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3346 (vs), 3166 (s), 2654 (m), 1701 (vs), 1627 (m), 1527 (m), 1447 (m), 1403 (m), 1348 (s), 1263 (w), 1189 (s), 1155 (w), 1106 (vw), 1039 (vw), 967 (w), 907 (vw), 765 (m), 730 (vw), 637 (vw), 571 (w), 549 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3343 (1), 1697 (2), 1601 (2), 1582 (2), 1530 (6), 1493 (20), 1476 (27), 1453 (81), 1402 (52), 1376 (73), 1281 (8), 1191 (4), 1176 (4), 1157 (3), 1139 (3) 1138 (3), 1076 (101), 1059 (53), 969 (3), 944 (2), 915 (3), 766 (3), 746 (1), 723 (1), 582 (2), 180 (6), 405 (2), 371 (1), 285 (1), 180 (6), 120 (29), 89 (17), 66 (12); ^{1}H NMR (d_6 DMSO, 25 °C, ppm): δ = 7.82 (s, br), 6.20 (s, br); ^{13}C NMR (d_6 DMSO, 25 °C, ppm): δ = 168.3 (CN_4), 164.0 (CN_4), 160.5 ($C{=}O$); *m/z* (FAB^+): 90.1 $[CH_7N_4O]^+$; *m/z* (FAB^-): 181.1 $[C_2HN_{10}O]^-$; EA ($C_4H_{14}N_{18}O_3$, 362.15) calcd: N 69.59, C 13.26, H 3.90; found: N 68.54, C 13.69, H 3.76%; impact sensitivity: 3.5 J; friction sensitivity: 240 N; ESD: 0.5 J (at grain size <100 µm).

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