A Study of Cyanotetrazole Oxides and Derivatives thereof

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Abstract: In this work we report on the syntheses of energetic salts of cyanotetrazolate-1- and -2-oxides; this offers a unique ability to compare the effects of tetrazole 1- versus 2-oxidation. 5-Cyanotetrazolate-2-oxide can be synthesized by oxidation of the 5-cyanotetrazolate anion with Oxone, while the corresponding 1-oxide was synthesized by the rearrangement of azidoaminofurazan. Both chemical (multinuclear NMR, IR, and Raman spectroscopies, mass spectrometry, etc.) as well as explosive (impact, friction, and static sensitivities) properties are reported for these energetic salts. Calculated explosive performances using the EXPLO5 computer code are also reported. We furthermore detail the chemistry of these two anions, and their ability to form tetrazole-carboxamides, dihydro-tetrazines, and tetrazines. The ability to hydrolyze cyanotetrazole oxides to their amides was demonstrated by two copper complexes. Several crystal structures of these species are presented in addition to full chemical characterization. Finally, the unique 1,4,-bis(2-N-oxidotetrazolate)-1,2,4,5-tetrazine anion was characterized as an energetic material as its ammonium salt.

Keywords: crystal structures · energetic materials · N-oxides · tetrazines · tetrazoles

Introduction

The development of new energetic materials for practical use is an area of intense research.[1–5] Many strategies in the design of new energetic materials have been extensively explored, differing only in the source of energy content. Traditional energetic materials such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and TNT (2,4,6-trinitrotoluene) rely on the oxidation of a carbon backbone by oxygen present in the molecule, ring- or caged-strained compounds such as octanitrocubane or trinitroazetidine, which introduce additional energy content from their strained bonds and high heat of formation, or nitrogen-rich compounds, for which the energetic driving force originates from nitrogen–nitrogen double and single bonds to produce nitrogen gas.

However, these energetic strategies have drawbacks: nitroaromatics and nitramines are toxic,[6,7] compounds with excessive ring or cage strain have very long synthetic routes,[8,9] and nitrogen-rich compounds lose thermodynamic and mechanical stability as the number of nitrogen atoms per heterocycle or chain becomes too large.[10,11,12] A possible solution to the problem of stability of very nitrogen-rich compounds is the addition of a zwitterionic N-oxide to the nitrogen system. The removal of σ electron density can stabilize systems as is seen in 1,2,3,4-tetrazine dioxides,[13–15] and N-oxides also increase densities[16] and oxygen balances, thus leading to increased energetic performances. Additionally, the increased intermolecular interactions afforded by the very polar N-oxide often stabilize these materials towards physical impact, thereby making them safer to handle.[17,18] The utility of N-oxides is illustrated in the variety of energetic materials possessing this functionality such as 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO),[19] TKX50,[20] and dinitroazofuroxan (DDF)[21] (Figure 1).
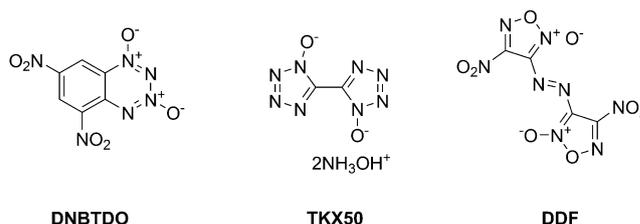

Figure 1. Energetic N-oxides.

Within the area of tetrazole-N-oxides we have previously detailed the preparation of salts of nitro-,[17] azido-,[18] and bistetrazole[20] oxides, and the general trends for N-oxides have held true; they are of higher density, lower sensitivity, and higher performance than the non-oxidized parent compounds; however, they possess a slightly lowered thermal stability. We have been limited previously by the lack of an easy comparison between 1- and 2-tetrazole oxides as nitro-

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and azidotetrazole are known as their 2-oxides, whereas bis-tetrazole is known as its 1-oxide. In this work, we detail the preparation and characterization of both salts of cyanotetrazole 1- and 2-oxides, thereby allowing for the comparison of the effect of N1- versus N2-oxidation. Additionally, we report on the reactions of cyanotetrazole oxides to give tetrazole oxides functionalized with carboxamide, 1,4-dihydro-1,2,4,5-tetrazines, and 1,2,4,5 tetrazine.

Results and Discussion

Synthesis

Prior to this work, the cyanotetrazolate-2-oxide anion was unknown. The preparation of the cyanotetrazolate-2-oxide anion was based on an extrapolation of our previous work.[17,18] An aqueous solution of sodium 5-cyanotetrazolate was oxidized with potassium peroxymonopersulfate (Oxone) overnight at 40 °C (Scheme 1). By pouring the reac-
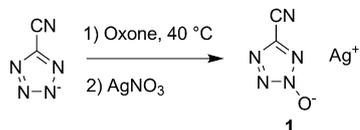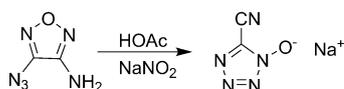

Scheme 1. Oxidation of the cyanotetrazolate anion.

tion mixture into acetone and filtering the precipitate, a crude solution of the cyanotetrazolate-2-oxide in acetone was obtained. After purification by recrystallization, the crude cyanotetrazolate-2-oxide salts were precipitated with silver nitrate, thus yielding pure silver cyanotetrazolate-2-oxide (1) as a white powder. In the case of the ammonium salt (2), extraction of the crude reaction mixture with ethyl acetate after the addition of aqueous sodium tributylammonium sulfate yielded the tributylammonium salt. Ion exchange led to the isolation of ammonium cyanotetrazolate-2-oxide (2) as colorless crystals.

Unlike the cyanotetrazolate-2-oxide, the cyanotetrazolate-1-oxide anion has been reported in one study[22] as the sodium salt from the reaction of azidoaminofurazan with sodium nitrite (Scheme 2). This sodium salt was precipitated as the silver salt (3) by addition of aqueous silver nitrate, or transformed to the ammonium salt (4) by ion exchange chromatography performed after extracting the tributylammonium salt from solution.

Using silver salts 1 and 3, metathesis reactions with aminoguanidinium chloride, diaminoguanidinium iodide, or triaminoguanidinium chloride gave the corresponding nitrogen-

Scheme 2. Rearrangement of azidoaminofurazane to the cyanotetrazolate-1-oxide anion.

rich salts (aminoguanidinium cyanotetrazolate-2-oxide (5), diaminoguanidinium cyanotetrazolate-2-oxide (6), triamino-guanidinium cyanotetrazolate-2-oxide (7), aminoguanidinium cyanotetrazolate-1-oxide (8), and triaminoguanidinium cyanotetrazolate-1-oxide (9)) of the cyanotetrazolate-1 and -2 oxides after filtering off the corresponding silver halide as by-product. Crystals were grown by the slow diffusion of ether into a methanolic solution of the salt.

When copper(II) chloride was attempted to be reacted with silver salts 1 and 3, instead of obtaining the desired salt of cyanotetrazolate oxide, the cyano group of the tetrazole was found to hydrolyze to the amide, thus yielding the copper salts of the carboxamidetetrazole oxides as the dihydrates (Scheme 3). These salts, unlike the other salts, were heated during synthesis, and we suspect that this is the reason for hydrolysis. The hydrolysis of cyanoazoles in aqueous media has been observed previously.[23]
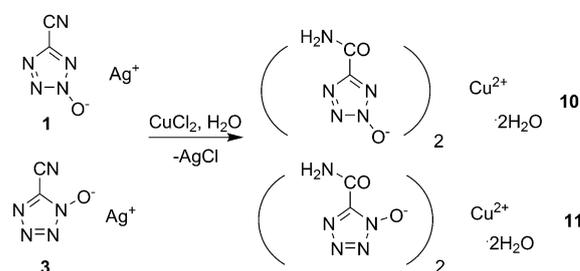
Scheme 3. Hydrolysis of cyanotetrazole oxides to their amides.

It is known in the literature[24] that upon treatment of 5-cyanotetrazole with hydrazine in ethanol, a dihydrotetrazine is formed, thereby bridging the tetrazole rings. When cyano-tetrazole 1- and 2-oxides were protonated with nitric acid yielding 5-cyano-2-hydroxytetrazole and 5-cyano-1-hydroxy-tetrazole, the subsequent treatment with hydrazine gave the corresponding dihydrotetrazines as their hydrazinium salts (12, 13; see Scheme 4).

Compounds 12 and 13 were then protonated with hydro-chloric acid in water yielding the 1- and 2-hydroxy species as hydrates, 14·2H$_2$O and 15·H$_2$O. Determination of hydration waters was based on 'best fit' of the elemental analyses. 14·2H$_2$O and 15·H$_2$O were then deprotonated with ammonia yielding ammonium salts 16 and 17·H$_2$O, respectively. With
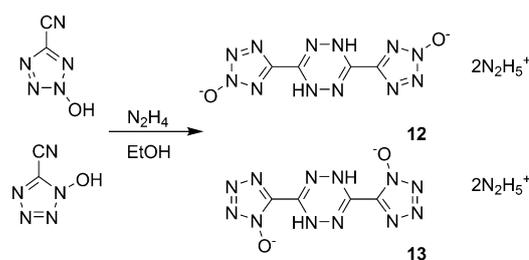
Scheme 4. Formation of dihydrotetrazines.

the free dihydrotetrazines **14·2 H₂O** and **15·H₂O** in hand, the goal was to oxidize them to the corresponding tetrazines (Scheme 5).
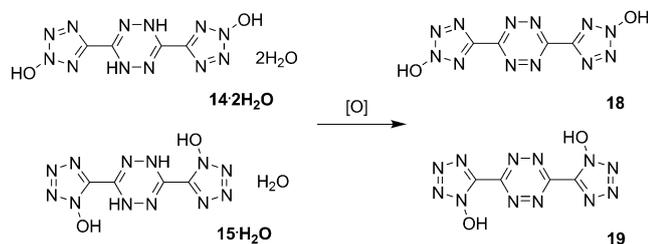
Scheme 5. Oxidation of dihydrotetrazines to tetrazines.

Initially, **18** was prepared by bubbling NO₂ through an aqueous solution of **14·2 H₂O**. The solution instantly turned deep red due to formation of the tetrazine; however, analysis of the NMR spectra indicated extensive decomposition. When a dilute solution of NO₂ in acetonitrile was added to a slurry of **14·2 H₂O** in acetonitrile until no more solid dissolved, a product of higher purity was obtained. The ¹³C NMR spectrum only possessed two resonances, whereas in the ¹H NMR spectrum decomposition was still observed, thus precluding assignment. After addition of the NO₂ solution in acetonitrile, the remaining insolubles were filtered off and the red filtrate was concentrated. Unfortunately, **18** proved to be hygroscopic, and therefore it was dried under high vacuum at 40 °C. The obtained red material, when freshly dried, was a highly sensitive explosive: it exploded when a 150 g hammer impacted it from only 1 cm. By reacting this material with aqueous ammonia, the ammonium salt **20** was obtained and fully characterized. Crystals of **20** were grown by diffusing ether into a methanolic solution of **20**. The oxidation of **15·H₂O** to **19** by a similar methodology proved unsuccessful. Oxidation in a manner analogous to that of the 2-oxide led to a red material that lost color upon standing in MeOH or DMSO and decomposed. Attempts using chlorine or ozone as oxidants also failed.

Spectroscopy

Multinuclear NMR spectroscopy, especially ¹³C and ¹⁵N NMR spectroscopy proved to be a useful tool for the characterization of the energetic anions and their salts. In the case of the cyanotetrazolate-1- and 2-oxide anions, the resonance of the tetrazole ring carbon was more downfield for the 2-oxide at 131.1 ppm versus 123.7 ppm for the 1-oxide. The cyano groups exhibit less of a shift difference, with resonances at 112.3 ppm and 110.5 ppm for the 2-oxide and the 1-oxide, respectively. When the cyano groups of both compounds were cyclized to give salts of dihydrotetrazines (**12**, **13**, **16**, and **17**), the 2-oxide possesses resonances at 148.1 and 140.5 ppm and the 1-oxide at 140.4 and 134.3 ppm. Unfortunately, these resonances are too similar to assign them to the tetrazole oxide and to the dihydrote-

trazine, respectively. After oxidation of the dihydrotetrazine tetrazole-2-oxide and formation of the ammonium salt **20**, the carbon resonances are found at 158.2 and 150.9 ppm. ¹⁵N NMR spectroscopy was also performed, and the assignment of resonances was made based on a calculated spectrum using MPW1PW91/aug-cc-pVDZ, Gaussian 09.[25] All resonances were readily assigned with the exception of N2 and N3 in the cyanotetrazolate-2-oxide anion, for which the resonances were too similar to assign them with certainty. Assignments are presented in Figure 2.
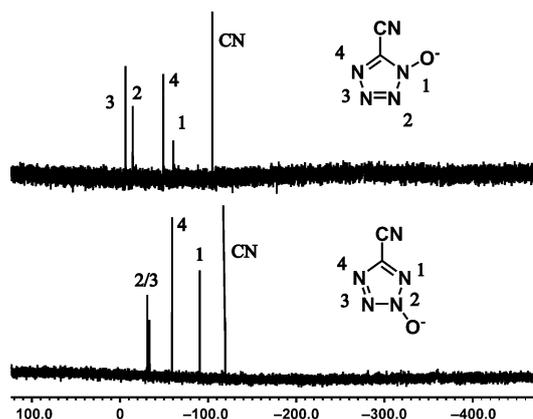

Figure 2. ¹⁵N NMR spectrum of cyanotetrazolate-1 and −2-oxides.

The IR and Raman spectra of all cyanotetrazolate oxide salts were collected and assigned using frequency analysis from an optimized structure of B3LYP/cc-pVDZ calculations using the Gaussian 09 software[25]. All calculations were performed at the DFT level of theory; the gradient-corrected hybrid three-parameter B3LYP[26,27] functional theory was used with a correlation-consistent *p*-VDZ basis set.[28–31]

In the IR spectra, the cyanotetrazolate-1-oxide salts generally contain a strong band around 1406 cm⁻¹. The calculated value for this band is 1503 cm⁻¹ and it arises from N−O stretching. At 2247–2255 cm⁻¹ (calc. 2312 cm⁻¹), the C≡N stretch is seen. At 1429 cm⁻¹ (calc. 1458 cm⁻¹), N1-C1-N4 symmetric tetrazole ring deformation occurs. Finally, the N1-C1-N4 asymmetric tetrazole deformation with minor N-O stretching occurs at 1241–1257 cm⁻¹ (calc. 1278 cm⁻¹).

The IR spectrum of the cyanotetrazolate-2-oxides possesses an N−O O stretch between 1430 and 1674 cm⁻¹ (calc. 1533 cm⁻¹). The C≡N stretch occurs at 2251–2259 cm⁻¹ (calc. 2315 cm⁻¹). Between 950 and 979 cm⁻¹ (calc. 950 cm⁻¹), the tetrazole N2-N3 stretch is observed, and finally between 1133 and 1360 cm⁻¹ (calc. 1401 cm⁻¹), the N3-N4 stretch is seen.

The Raman spectra of all salts of cyanotetrazolate-1-oxide adopt a characteristic pattern of two bands of high intensity. The band between 2249 and 2257 cm⁻¹ (calc. 2312 cm⁻¹) is caused by C≡N stretching. The final stretching occurring at 1458–1465 cm⁻¹(calc. 1458 cm⁻¹) corresponds to a N1-C1-N4 symmetric tetrazole ring deformation.

In the Raman spectra of the cyanotetrazolate-2-oxide salts, a characteristic pattern of three diagnostic bands is observed. The strongest band at 2256–2261 cm^{-1} (calc. 2315 cm^{-1}) arises from the C≡N stretch. The second band corresponds to a tetrazole N2-N3 stretch and occurs between 1001 and 1019 cm^{-1} (calc. 950 cm^{-1}). The final diagnostic stretch ranging from 1436 to 1442 cm^{-1} (calc. 1407 cm^{-1}) belongs to C1-N4 asymmetric tetrazole deformation.

Single Crystal X-ray Analysis

Several herein described compounds (**2**, **4**, **5**, **6**, **7**, **9**, **10**, **11**, and **20**) were also characterized by low-temperature single-crystal X-ray diffraction. Selected data and parameters of the measurements and solutions are gathered in Tables S1 and S2 in the Supporting Information.

Ammonium 2-oxido-5-cyanotetrazolate (**2**) crystallizes in the non-centrosymmetric space group $Pca2_1$ with four cation/anion pairings in the unit cell. In comparison with the corresponding ammonium 1-oxido-5-cyanotetrazolate (**4**) (monoclinic, $P2_1/c$), **2** has a slightly higher density of 1.553 g cm^{-3} (vs. 1.526 g cm^{-3} for **4**). Basically, the oxido-cyanotetrazolate anions are formed as planar anions, in agreement with non-oxidized 2H-cyanotetrazole.[32] Within the planar aromatic tetrazolate rings, bond lengths between single and double bonds are observed. The bond lengths between the cyano group and the C1 atom lie between 1.42 and 1.44 Å, while the CN bond length in the cyano group is between 1.13 and 1.15 Å. These two bond lengths are not affected by deprotonation as well as oxygenation of the tetrazole ring system. Detailed bond lengths and angles are gathered in Table S3 in the Supporting Information.

The structures of **2** and **4** are dominated by several strong hydrogen bonds involving all hydrogen atoms of the ammonium cations coordinating to the atoms N2, N4, and O1 (**2**) and N1, N2, N3, N4, and O1 (**4**), respectively. Depictions of the molecular units are presented in Figures 3 and 4.

Amino- (**5**) and diaminoguanidinium 2-oxido-5-cyanotetrazolate (**6**), shown in Figures 5 and 6, both crystallize mon-

Figure 4. Molecular unit of **4** and its labeling scheme. Ellipsoids are drawn at the 50 % probability level.

oclinic in the space groups $P2_1/n$ and $P2_1/c$, respectively. The diaminoguanidinium salt **6** (1.534 g cm^{-3}) shows a slightly higher density in comparison to **5** (1.504 g cm^{-3}). Both structures again are dominated by an intense hydrogen bond network.

The structures of triaminoguanidinium 1- (**9**) and 2-oxido-5-cyanotetrazolate (**7**) could also be determined. The triaminoguanidinium cations follow structures published numerously in the literature such as, for example, triaminoguanidinium nitrate.[33] The densities of 1.550 g cm^{-3} (**7**) and 1.583 g cm^{-3} (**9**) are higher than those of **2** and **4–6**. The molecular units of both structures are shown in Figures 7 and 8.

Figure 5. Molecular unit of **5** and its labeling scheme. Ellipsoids are drawn at the 50 % probability level.

Figure 3. Molecular unit of **2** and its labeling scheme. Ellipsoids are drawn at the 50 % probability level.

Figure 6. Molecular unit of **6** and its labeling scheme. Ellipsoids are drawn at the 50 % probability level.
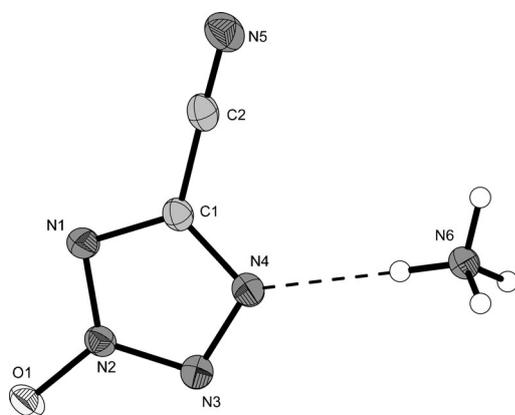
Figure 7. Molecular unit of **7** and its labeling scheme. Ellipsoids are drawn at the 50% probability level.

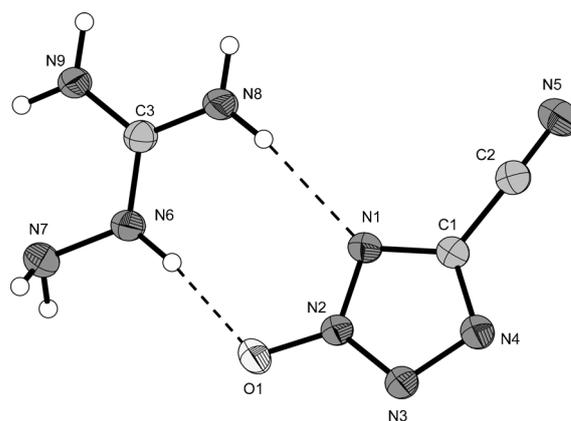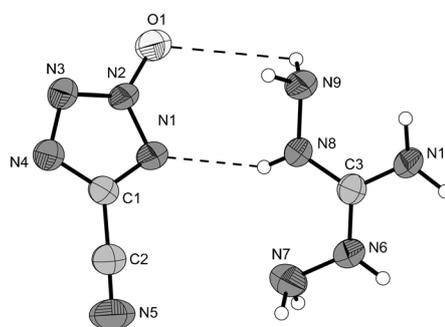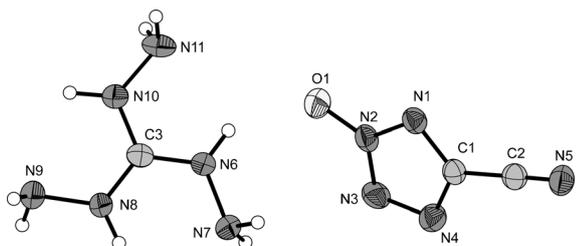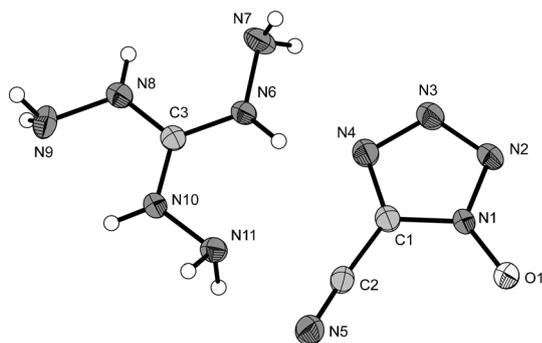Figure 8. Molecular unit of **9** and its labeling scheme. Ellipsoids are drawn at the 50% probability level.

Single crystals could be obtained after the reaction of 1- and 2-oxido-5-cyanotetrazolate with copper sulfate. In both cases, the corresponding Cu^{II} complexes of the hydrolyzed CN moiety were formed as dihydrates. In both compounds, an expected distorted coordination sphere of d^9 copper centers was observed; however, the coordination modes of the oxido-tetrazolates were different. In the case of **10** (Figure 9), the bidentate coordination (5-membered ring) is formed by the ring nitrogen atom N1 and the carboxy oxygen atom O1. In the case of **11** (Figure 10), a six-membered ring is formed by coordination of the N-oxide oxygen atom O2 as well as the carboxy oxgen atom O1. The coordi-
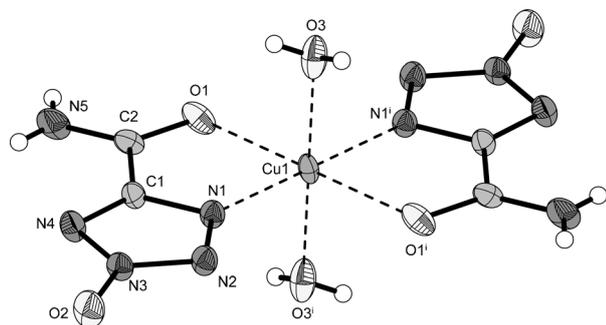
Figure 9. Molecular unit of **10** and its labeling scheme. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Cu1–N1 1.957(2), Cu1–O3 2.181(3), Cu1–O1 2.191(2), N1–N2 1.326(3), N1–C1 1.335(3), O2–N3 1.284(3), N3–N2 1.330(3), N3–N4 1.337(3), N5–C2 1.312(4), O1–C2 1.245(4), N4–C1 1.327(4), C1–C2 1.489(4); selected coordination angles [°]: N1-Cu1-O3 90.65(10), N1-Cu1-O1 78.48(8), O3-Cu1-O1 92.32(9).
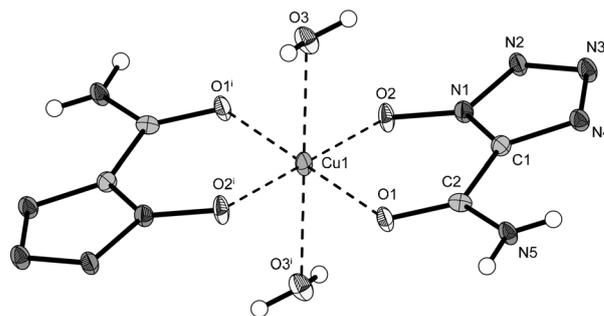
Figure 10. Molecular unit of **11** and its labeling scheme. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Cu1–O2 1.935(2), Cu1–O1 1.980(2), Cu1–O3 2.396(3), N5–C2 1.313(4), N4–C1 1.335(4), N4–N3 1.345(3), N3–N2 1.305(4), N2–N1 1.338(3), N1–O2 1.328(3), N1–C1 1.341(4), O1–C2 1.245(4), C2–C1 1.481(4); selected coordination angles [°]: O2-Cu1-O1 94.62(9), O2-Cu1-O3 89.80(10), O1-Cu1-O3 92.51(9).

nation sphere of complex **11** is a typical example of an elongated octahedron formed by Jahn–Teller distortion and described for several copper(II) tetrazolates in the literature.[34]

Compound **20** could only be obtained crystalline as its trihydrate. A depiction of a molecular unit is given in Figure 11. The asymmetric unit consists of two transected
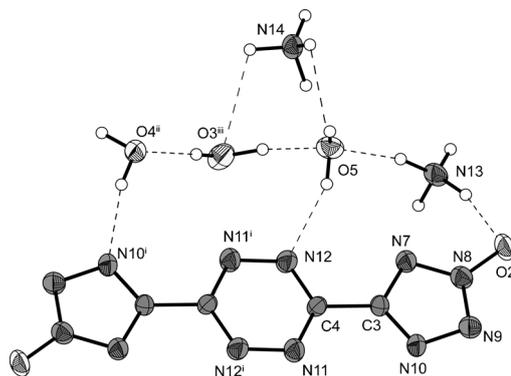
Figure 11. View on one molecular unit of **20** and its labeling scheme. Ellipsoids are drawn at the 50% probability level.

dianions. All water and ammonium protons participate in hydrogen bonds. The density of **20** (1.627 gcm^{-3}), which crystallizes in the triclinic space group $P\bar{1}$, is the highest observed for the crystalline CHNO compounds within this work. The oxido-tetrazolate dianions have a planar structure similar to that of recently published energetic salts of the 3,6-bis(tetrazole-5-ylate)-1,2,4,5-tetrazine dianion.[35] The dianions are orientated in bands connected by hydrogen bonds involving crystal water and atom O4. Gaps are filled with the ammonium cations and two further crystal water molecules, as shown in Figure 12.

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Figure 12. View on the layer-like packing of **20**. One unit cell is drawn.

Table 1. CBS-4M results and gas-phase enthalpies

	Formula	$-H^{298[a]}$/a.u.	$\Delta_f H$ (g)[b] [kJ mol^{-1}]
HCT2X[c]	C_2HN_5O	425.116700	484.7
CT2X$^{-[d]}$	$C_2HN_5O^-$	424.625696	240.3
HCT1X[e]	$C_2HN_5O^-$	425.105680	513.6
CT1X$^{-[f]}$	$C_2N_5O^-$	424.615667	266.7
TT2X$^{2-[g]}$	$C_4N_{12}O_2^{2-}$	958.510314	864.6
NH$_4$ $^{+[h]}$	NH_4^+	56.796608	635.8
AG$^{+[i]}$	$CH_7N_4^+$	260.701802	671.6
DAG$^{+[j]}$	$CH_8N_5^+$	315.949896	772.7
TAG$^{+[k]}$	$CH_9N_6^+$	371.197775	874.3

[a] CBS-4M enthalpy at room temperature; [b] calculated gas-phase heat of formation by using the atomization equation; [c] cyanotetrazolate-2-oxide, protonated; [d] cyanotetrazolate-2-oxide, deprotonated; [e] cyano-tetrazolate-1-oxide, protonated; [f] cyanotetrazolate-1-oxide, deprotonated; [g] 1,4,-bis(2-N-oxidotetrazolate)-1,2,4,5-tetrazine; [h] ammonium; [i] aminoguanidinium cation; [j] diaminoguanidinium cation; [k] triamino-guanidinium cation.

Energetic Properties

Often, energetic materials tend to explode in bomb calorimetric measurements. Consequently, doubtful combustion energies can potentially be obtained. Therefore, heats of formation of energetic materials are mostly calculated theoretically. In our group, we combine the atomization energy method (Eq. 1) with CBS-4M electronic energies (Table 1), which has been shown suitable in many recently published studies.[36] CBS-4M energies of the atoms, cations, and anions were calculated with the Gaussian 09 (revision A1) software package[25] and checked for imaginary frequencies. Values for $\Delta_f H°$ (atoms) were taken from the NIST database.[37]
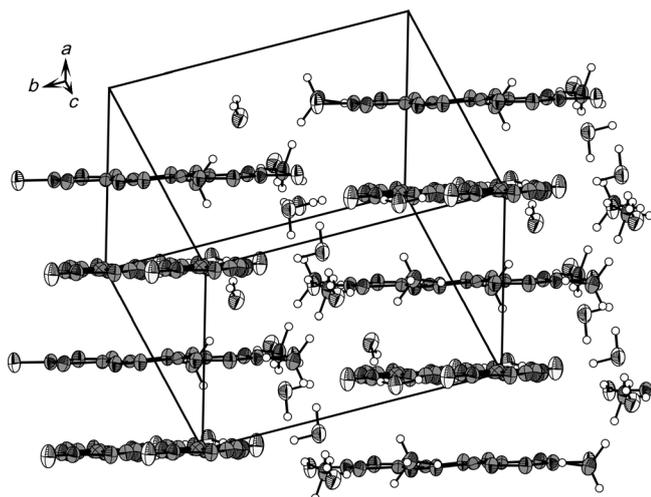
$$\Delta_f H°_{(g, M, 298)} = H_{(Molecule, 298)} - \sum H°_{(Atoms, 298)} + \sum \Delta_f H°_{(Atoms, 298)}$$
(1)

For calculation of the solid-state energy of formation (Table 2) of **2**, **4–7**, **9**, and **20**, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding molecular volumes (obtained from X-ray elucidations) according to the equations provided by Jenkins and Glasser.[38]

Only these compounds were calculated as they have experimental densities for energetic performance calculations. With the calculated lattice enthalpy (Table 2), the gas-phase enthalpy of formation was converted into the solid-state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid-state energies of formation (ΔU_m) according to Eq. 2 (Table 2).

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

in which Δn denotes the change of moles of gaseous components.

Density is one of the most important parameters for performance calculations. Therefore, only compounds with precise X-ray densities have been studied for their performances. The detonation and propulsion parameters of **2**, **4–7**, **9**, and **20** were calculated using the program EXPLO5 V5.05[39] and are gathered in Table 3. The program is based on the steady-state model of equilibrium detonation and uses the Becker–Kistiakowsky–Wilson equation of state (BKW E.O.S) for gaseous detonation products and Cowan–Fickett E.O.S. for solid carbon.[40] The program is designed to enable the calculation of detonation parameters at the Chapman–Jouguet point. The calculations were performed

Table 2. Solid state energies of formation ($\Delta_f U°$).

	$\Delta_f H°$ (g)[a] [kJ mol^{-1}]	V_M [b]/ nm^3	U_L[c] [kJ mol^{-1}]	ΔH_L[d] [kJ mol^{-1}]	$\Delta_f H°$(s)[e] [kJ mol^{-1}]	Δn[f]	$\Delta_f U°$(s)[g] [kJ mol^{-1}]	Formula	M [g mol^{-1}]	$\Delta_f U°$(s)[h] [kJ kg^{-1}]
2	876.1	0.137	559.0	563.9	312.2	5.5	325.9	$C_2H_4N_6O$	128.09	2543.3
4	902.5	0.139	556.2	561.2	341.3	5.5	354.9	$C_2H_4N_6O$	128.09	2770.3
5	911.9	0.204	502.0	507.0	404.9	8.5	426.0	$C_3H_7N_9O$	185.15	2300.3
6	1013.0	0.217	494.4	499.3	513.6	9.5	537.2	$C_3H_8N_{10}O$	200.16	2683.0
7	1114.6	0.231	486.4	491.4	623.2	10.5	649.2	$C_3H_9N_{11}O$	215.18	3016.5
9	1140.9	0.226	489.1	494.0	646.9	10.5	672.9	$C_3H_9N_{11}O$	215.18	3126.6
20	1411.5*	0.318	1437.4	1452.3	−40.8	16.5	0.1	$C_4H_{14}N_{14}O_5$	338.24	0.4

[a] Gas-phase enthalpies of formation (those of the ionic compounds are taken as the respective sums of the non-interacting component ions);* gas-phase enthalpy of three water molecules were subtracted; [b] molecular volume of the molecular unit in the crystal structure; [c] lattice energy calculated by the Glasser–Jenkins equation; [d] lattice enthalpy calculated by the Glasser–Jenkins equation; [e] solid-state molar heat of formation; [f] change of moles of gaseous components; [g] molar energy of formation; [h] energy of formation (mass-dependent).

Table 3. Energetic properties and detonation parameters of **2**, **4–7**, **9**, and **20**.

	2	4	5	6	7	9	20	TNT
Formula	$C_2H_4N_6O$	$C_2H_4N_6O$	$C_3H_7N_9O$	$C_3H_8N_{10}O$	$C_3H_9N_{11}O$	$C_3H_9N_{11}O$	$C_4H_{14}N_{14}O_5$	$C_7H_5N_3O_6$
Molecular Mass [$g mol^{-1}$]	128.09	128.09	185.15	200.16	215.18	215.18	338.24	227.13
IS [J][a]	15	35	40	40	40	40	40	15[41]
FS [N][b]	216	360	324	324	324	216	240	353
ESD-test [J][c]	0.30	0.75	1.5	0.50	0.55	0.50	0.50	3.5
N [%][d]	65.61	65.61	68.09	69.98	71.60	71.60	57.97	18.50
Ω [%][e]	−62.45	−62.45	−73.54	−71.93	−70.63	−70.63	−47.30	−73.96
$T_{dec.}$ [°C][f]	184	172	228	152	160	150	189	290
Density [$g cm^{-3}$][g]	1.554	1.526	1.504	1.534	1.550	1.583	1.627	1.713(100 K)[42]
$\Delta_f H_m°$ [$kJ mol^{-1}$][h]	325.9	354.9	426.0	537.2	649.2	672.9	−40.8	−55.5
$\Delta_f U°$ [$kJ kg^{-1}$][i]	2543.3	2770.3	2300.3	2683.0	3016.5	3126.6	0.4	−168.0
EXPLO5.05:								
$-\Delta_E U°$ [$kJ kg^{-1}$][j]	4609	4831	3957	4277	4559	4666	3715	5258
T_E [K][k]	3288	3412	2842	2971	3060	3084	2746	3663
p_{CJ} [kbar][l]	222	220	196	219	237	251	227	235
D [$m s^{-1}$][m]	7749	7730	7451	7790	8044	8214	7799	7459
Gas vol. [$L kg^{-1}$][n]	762	762	771	788	803	803	840	569
I_S [s][o]	222	228	207	218	227	229	195	205

[a] impact sensitivity (BAM drop hammer, 1 of 6); [b] friction sensitivity (BAM friction tester, 1 of 6); [c] electrostatic discharge device (OZM); [d] nitrogen content; [e] oxygen balance;[43] [f] decomposition temperature from DSC ($\beta = 5$°C); [g] estimated from X-ray diffraction; [h] calculated (CBS-4M) heat of formation; [i] calculated energy of formation; [j] Energy of explosion; [k] explosion temperature; [l] detonation pressure; [m] detonation velocity; [n] assuming only gaseous products; [o] specific impulse calculated at isobaric (60 bar) rocket conditions.

using the maximum densities according to the crystal structures at low temperatures and the calculated energies of formation.

With respect to their detonation performance the best values were obtained for triaminoguanidinium salts **7** and **9**, with **9** being slightly higher (8044 and 8214 m s^{-1}, respectively), thus indicating higher performance for the 1-oxides. However, when ammonium salts **2** and **4** are compared, there is no appreciable difference between the two (7749 and 7730 m s^{-1}, respectively). All compounds prepared are of comparable or higher performance than trinitrotoluene (TNT), but lower than those of the commonly used military explosives like hexogen (RDX) and octogen (HMX).

We also calculated the specific impulse I_S (using the pure compound at 60 bar isobaric rocket conditions), which can be related to the potential use as propellant ingredient. The highest I_S was computed for compounds **4**, **7**, and **9** (228, 227, and 229 s, respectively).

The sensitivities of all compounds were determined by standard methods (see the Experimental Section). The only highly sensitive compound is compound **18**, which when completely dry can explode from only slight impacts. However, due to its high hygroscopicity, this compound's sensitivity rapidly decreases upon standing at ambient conditions. The remainder of compounds in this work are of much lower sensitivity, generally being classified as "less sensitive" to "sensitive" energetic materials according to the UN Recommendations on the Transport of Dangerous Goods.[44]

Conclusions

The direct oxidation of the cyanotetrazolate anion with Oxone gave the cyanotetrazolate-2-oxide anion. This, along with the known cyanotetrazolate-1-oxide gave energetic salts of both oxide-containing anions after metathesis reactions. These nitrogen-rich salts show energetic performances in the range of TNT; however, only salts **2** and **5** show thermal stabilities above 180°C. NMR, IR, and Raman spectroscopies proved useful for characterizing these materials. In the presence of copper, the cyano group of both the 1- and 2-oxides hydrolyze to the corresponding carboxamide. The protonated forms of both cyanotetrazolate-1- and 2-oxides were able to form dihydrotetrazines upon reaction with hydrazine. In the case of the 2-oxide, the dihydrotetrazine can be oxidized to the tetrazine, the ammonium salt of which was fully characterized, illustrating the unique heterocyclic system containing both tetrazole oxides and a 1,2,4,5-tetrazine ring. These compounds may provide base materials or synthetic strategies to new energetic materials.

Experimental Section

General

All reagents and solvents were used as received (Sigma–Aldrich, Fluka, and Acros Organics) unless stated otherwise. Sodium cyanotetrazolate-1-oxide was prepared according to the literature procedure.[22] Melting and decomposition points were measured with a Linseis PT10 differential scanning calorimeter using heating rates of 5°C min^{-1}. ^{1}H, ^{13}C and ^{15}N NMR spectra were measured with a JEOL Eclipse 270 or 400 MHz instrument. All chemical shifts are given in ppm relative to TMS (^{1}H, ^{13}C) or nitromethane (^{15}N). Infrared spectra were measured with a Perkin–Elmer FT-IR Spectrum BXII instrument equipped with a Smith Dura SampIIR II ATR unit. Transmittance values are described as strong (s), medium (m), and weak (w). Mass spectra were measured on a JEOL MStation JMS 700 instrument. Raman spectra were measured with a Perkin–Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported as percentages of the most intensive peak and are given in parentheses. Elemental analyses were performed with a Netsch STA 429 simultaneous

thermal analyzer. Sensitivity data were determined using a BAM drop hammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using the electric spark tester ESD 2010 EN (OZM Research) operating with the "Winspark 1.15" software package. XRD was performed on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at low temperature (173 K). The data collection and reduction was carried out using the CrysAlisPro software.[45] The structures were solved either with SHELXS-97[46] or SIR-92,[47] refined with SHELXL-97[48], and finally checked using the PLATON[49] software integrated in the WINGX[50] software suite. All hydrogen atoms were found and freely refined. Friedel pairs of non-centrosymmetric space groups have been merged using the MERG3 command. The absorptions were corrected with a Scale3 Abspack multi-scan method.[51] CCDC 899950 (**2**), CCDC 899952 (**4**), CCDC 899957 (**5**), CCDC 899956 (**6**), CCDC 899951 (**7**), CCDC 899953 (**9**), CCDC 899955 (**10**), CCDC 899954 (**11**), and CCDC 899949 (**20**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CAUTION! *The described compounds are energetic materials with sensitivity to various stimuli. While we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthened equipment) should be used at all times. Compound **18** is extremely sensitive when dry and should only be handled in small quantities or wet.*

*Silver cyanotetrazolate-2-oxide (**1**)*

Sodium cyanotetrazolate·1.5 H$_2$O (5 g, 34.7 mmol) was dissolved in 70 mL of distilled water, and potassium acetate (29.8 g, 304 mmol) was added. The solution was heated to 40 °C, and Oxone (66.8 g, 98 mmol) was added slowly. After stirring of the suspension for 20 h at 40 °C, the solution was poured into 1.6 L of acetone and precipitated salts were filtered off. After evaporation of the solvent under reduced pressure, the remaining solid was dissolved in ethanol. The insoluble residues were filtered off, and the filtrate was evaporated under vacuum. The colorless solid was dissolved in 100 mL of distilled water, and a solution of silver nitrate (5.9 g, 34.7 mmol) in 100 mL of distilled water was added in the dark while stirring. Still in the dark, the colorless suspension was stirred for 15 min, filtered, and washed with 20 mL of distilled water. After drying in the dark, **1** was obtained as a white solid (5.5 g, 73 %). DSC (5 °C min^{-1}): 224 °C (dec); IR: $\tilde{v} = 3627$ (w), 3464 (w), 2921 (m), 2242 (m), 1596 (w), 1441 (m), 1428 (m), 1403 (m), 1365 (s), 1340 (m), 1267 (w), 1225 (m), 1090 (m), 1013 (m), 812 (s), 710 cm^{-1} (s); ^{13}C NMR ([D$_6$]DMSO): $\delta = 132.0$ (s, 1C, CN$_4$O), 112.3 ppm (s, 1C, CN); MS (FAB$^-$) m/z: 110.0 (C$_2$N$_5$O); (FAB$^+$) m/z 107.0 (Ag); elemental analysis calcd (%) for AgC$_2$N$_5$O (217.92): C 11.02, N 32.14, H 0.00; found: C 11.32, N 31.96; H 0.00. BAM impact: 8 J; BAM friction: 240 N; ESD: 50 mJ.

*Ammonium cyanotetrazolate-2-oxide (**2**)*

Sodium cyanotetrazolate·1.5 H$_2$O (10 g, 69.4 mmol) was dissolved in 240 mL of distilled water. Next, potassium acetate (59.6 g, 608 mmol) was added and the solution heated to 40 °C. Subsequently, Oxone (120 g, 196 mmol) was added in small portions during the course of 1 h. The suspension was stirred for 20 h at 40 °C, followed by the addition of sufficient water to dissolve all solids. The solution was then allowed to slowly cool down to room temperature, and an excess of sodium tributylammonium sulfate (NaBu$_3$NHSO$_4$; 0.8 M, 300 mL) was added. The solution was extracted with ethylacetate (5 × 200 mL), and the combined organic phase was combined and dried over anhydrous magnesium sulfate followed by the evaporation of the solvent under vacuum to give a colorless oil. The oil was mixed with 12 mL of methanol, and the solution was passed through a column of Amberlyst 15 ion exchange resin loaded with ammonium ions. The colorless eluent was evaporated to dryness and recrystallized from acetonitrile to give ammonium 5-cyanotetrazolate-2-oxide as colorless crystals (4.9 g, 55 %) . DSC (5 °C min^{-1}): 176 °C (mp), 184 °C (dec); IR: $\tilde{v} = 3697$ (w), 3141 (m), 3020 (s), 2918 (w), 2890 (w), 2856 (w),

2544 (w), 2349 (w), 2259 (m), 2179 (w), 2136 (w), 1807 (w), 1708 (w), 1692 (m), 1591 (w), 1546 (w), 1472 (s), 1455 (w), 1438 (s), 1430 (s), 1401 (m), 1387 (m), 1370 (w), 1344 (s), 1226 (s), 1111 (w), 1073 (m), 1013 (m), 792 (m), 723 (m), 698 cm^{-1} (w); Raman (1064 nm): $\tilde{v} = 3047$ (3), 2261 (100), 1700 (1), 1484 (1), 1442 (21), 1389 (8), 1356 (1), 1228 (3), 1109 (14), 1078 (1), 797 (4), 607 (1), 725 (3), 575 (3), 501 (5), 486 (1), 343 cm^{-1} (1); ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.2$ ppm (brs, 4H, NH$_4$); ^{13}C NMR ([D$_6$]DMSO): $\delta = 132.6$ (s, 1C, CN$_4$O), 112.2 (s, 1C, CN); MS m/z: (FAB$^-$) 110.0 ppm (C$_2$N$_5$O); (FAB$^+$) m/z: 18.1 (NH$_4$); elemental analysis calcd (%) for C$_2$N$_6$H$_4$O (128.09): C 18.75, N 65.61, H 3.15; found: C 19.02, N 65.36, H 3.01; BAM impact: 15 J; BAM friction: 216 N; ESD: 300 mJ.

*Silver cyanotetrazolate-1-oxide (**3**)*

Sodium cyanotetrazolate-1-oxide (200 mg, 1.4 mmol) was dissolved in 10 mL of distilled water. Under constant stirring in the dark, a solution of silver nitrate (238 mg, 1.4 mmol) in 10 mL water was added, and **3** started to precipitate immediately. The light yellow suspension was stirred for 20 min, filtered under suction, and washed with distilled water. After drying in the dark, **3** was obtained as a white solid (220 mg, 72 %). DSC (5 °C min^{-1}): 201 (T_{dec}); IR: $\tilde{v} = 3619$ (w), 3448 (w), 2248 (w), 1572 (w), 1470 (s), 1444 (m), 1427 (m), 1413 (m), 1378 (w), 1330 (w), 1257 (s), 1241 (s), 1225 (w), 1208 (m), 1159 (w), 1096 (w), 1019 (w), 784 (s), 700 cm^{-1} (w); ^{13}C NMR ([D$_6$]DMSO): $\delta = 123.8$ (s); 110.7 ppm (s); MS (FAB$^-$) m/z: 110.0 (C$_2$N$_5$O$^-$); elemental analysis calcd (%) for AgC$_2$N$_5$O (217.92): C 11.02, H 0.00, N 32.14; found: C 11.23; H 0.00, N 31.52; BAM impact: > 4 J; BAM friction: 120 N; ESD: 80 mJ.

*Ammonium cyanotetrazolate-1-oxide (**4**)*

Sodium tributylammoniumsulfate (30 mL, 0.8 M, 24 mmol) was added to a solution of sodium cyanotetrazolate-1-oxide (0.93 g, 6.6 mmol) in 20 mL of distilled water. After stirring for 30 min, the solution was extracted six times with 15 mL of ethyl acetate. The combined ethyl acetate fractions were then evaporated under reduced pressure. The remaining slightly yellow oil was dissolved in methanol and passed through a column of Amberlyst 15 ion-exchange resin loaded with ammonium cations at a slow rate (ca. 1.5 h). The yellow eluent was evaporated to dryness and recrystallized from 1-propanol to yield **4** as a white solid (0.205 g, 24 %). DSC (5 °C min $^{-1}$): 160 °C (mp), 172 °C (dec); IR: $\tilde{v} = 3171$ (w), 2995 (w), 2829 (w), 2255 (w), 2159 (w), 1695 (w), 1534 (w), 1463 (m), 1429 (s), 1406 (vs), 1241 (s), 1219 (m), 1148 (w), 1080 (w), 1007 (w), 768 (m), 692 cm^{-1} (w); Raman (1064 nm): $\tilde{v} = 2257$ (100), 1466 (50), 1415 (2), 1392 (2), 1246 (3), 1221 (20), 1147 (10), 1091 (6), 1010 (14), 771 (15), 638 (8); 547 (3), 495 (10), 413 (2), 1079 (1), 182 (21), 109 (11), 718 (2), 697 cm^{-1} (1); ^{13}C NMR ([D$_6$]DMSO): $\delta = 123.9$ (s, -CN$_4$); 110.8 ppm (s, -CN); ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.14$ ppm (s, 4H, NH$_4^+$); MS (FAB$^+$) m/z: 18.0 (NH$_4^+$); (FAB$^-$) m/z: 110.0 (C$_2$N$_5$O$^-$); elemental analysis calcd (%) for NH$_4$C$_2$N$_5$O (128.09): C 18.75, H 3.15, N 65.61; found: C 19.26, H 2.96, N 64.68; BAM impact: 35 J; BAM friction: 360 N; ESD: 0.75 J.

*Aminoguanidinium cyanotetrazolate-2-oxide (**5**)*

To a stirred solution of aminoguanidinium chloride (127 mg, 1.15 mmol) in 20 mL of distilled water, finely powdered **1** (250 mg, 1.15 mmol) was added. The suspension was stirred for 30 min and was filtered in the dark. The filtrate was evaporated to dryness to give **5** as colorless crystals (197 mg, 93 %). DSC (5 °C min^{-1}): 228 °C (dec); IR: $\tilde{v} = 3540$ (w), 3321 (m), 3262 (m), 3158 (m), 2869 (w), 2774 (w), 2353 (w), 2256 (m), 2198 (w), 1998 (w), 1660 (s), 1613 (w), 1461 (w), 1434 (w), 1421 (w), 1393 (w), 1360 (m), 1326 (w), 1243 (m), 1213 (w), 1512 (w), 1106 (w), 1070 (w), 1049 (w), 1011 (w), 973(w), 953 (w), 824 (w), 798 (w), 771 (w), 741 (w), 718 (w), 672 cm^{-1} (w); Raman (1064 nm): $\tilde{v} = 3367$ (1), 3334 (1), 3274 (4), 3232 (1), 2259 (100), 1683 (3), 1620 (2), 1569 (1), 1436 (30), 1399 (1), 1379 (1), 1238 (1), 1217 (2), 1095 (10), 1074 (4), 1019 (43), 959 (6), 802 (6), 719 (2), 614 (3), 571 (7), 518 (2), 502 (8), 484 (4), 337 cm^{-1} (2); ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.63$ (s, 1H, C-NH-N), 7.37 (brs, 2H, C-NH_2), 7.04 (brs, 2H, C-NH_2), 4.77 ppm (s, 2H, N-NH_2); ^{13}C NMR ([D$_6$]DMSO): $\delta = 159.4$ (s, 1C, C(NH$_2$)$_2$(NHNH$_2$), 132.0 (s, 1C, CN$_4$O),

112.6 ppm (s, 1C, CN); MS (FAB$^-$) m/z: 110.0 (C$_2$N$_5$O); (FAB$^+$) m/z: 75.1 (CN$_4$H$_7$); elemental analysis calcd (%) for CN$_4$H$_7$C$_2$N$_5$O (200.16): C 19.46, N 68.09, H 3.81; found: C 19.07, N 64.00, H 3.62. BAM impact: 40 J; BAM friction: 324 N; ESD: 1.5 J.

Diaminoguanidinium cyanotetrazolate-2-oxide (6)

Finely powdered **1** (250 mg, 1.15 mmol) was added to a solution of diaminoguanidinium iodide (249 mg, 1.15 mmol) in 20 mL of distilled water. The suspension was slowly shaken by hand for 15 min and filtered in the dark. The filtrate was evaporated to dryness to yield **6** as colorless crystals (193.6 mg, 84%). DSC (5°Cmin^{-1}): 135°C (mp), 152°C (dec); IR: $\tilde{\nu}$ = 3310 (w), 3234 (s), 3174 (s), 3000 (w), 2889 (w), 2251 (m), 1986 (w), 1913 8w), 1736 (w), 1668 (s), 1649 (w), 1596 (w), 1461 (w), 1436 (m), 1421 (w), 1394 (m), 1358 (s), 1272 (w), 1232 (m), 1215 (w), 1177 (m), 1120 (w), 1066 (w), 968 (s), 930 (w), 800 (m), 767 (m), 713 cm^{-1} (w); Raman (1064 nm): $\tilde{\nu}$ = 3791 (2), 3341 (1), 3240 (7), 2256 (100), 1689 (2), 1637 (3), 1437 (24), 1409 (3), 1367 (1), 1322 (1), 1234 (2), 1184 (4), 1090 (12), 1069 (2), 1010 (38), 931 (9), 802 (6), 719 (2), 572 (7), 549 (3), 499 (11), 479 (4), 396 (1), 366 (2), 265 cm^{-1} (4); ^{1}H NMR ([D$_6$]DMSO): δ = 8.54 (br s, 2H, C-NH-NH$_2$), 7.13 (s, 2H, C-NH_2), 4.58 ppm (s, 4H, N-NH_2); ^{13}C NMR ([D$_6$]DMSO): δ = 160.3 (s, 1C, C(NH$_2$)(NHNH$_2$)$_2$), 131.6 (s, 1C, CN$_4$O), 112.8 ppm (s, 1C, CN); MS (FAB$^-$) m/z: 110.0 (C$_2$N$_5$O); (FAB$^+$) m/z: 90.0 (CN$_5$H$_8$); elemental analysis calcd (%) for CN$_5$H$_8$C$_2$N$_5$O (200.16): C 18.00, N 69.98, H 4.03; found: C 18.55, N 67.93, H 4.01. BAM impact: 40 J; BAM friction: 324 N; ESD: 500 mJ.

Triaminoguanidinium cyanotetrazolate-2-oxide (7)

Finely powdered **1** (250 mg, 1.15 mmol) was added to a solution of triaminoguanidinium chloride (161.2 mg, 1.15 mmol) in 20 mL of distilled water in the dark. The suspension was carefully shaken for 15 min, filtered, and rinsed with 10 mL of distilled water in the dark. The filtrate was evaporated to yield **7** as colorless crystals (214.2 mg, 87%). DSC (5°C min^{-1}): 149°C (m.p.), 166°C (dec); IR: $\tilde{\nu}$ = 33614 (w), 3325 (w), 3208 (m), 3119 (w), 2354 (w), 2327 (w), 2256 (m), 1723 (w), 1674 (s), 1587 (w), 1554 (w), 1437 (m), 1400 (m), 1372 (w), 1332 (m), 1246 (w), 1224 (w), 1207 (w), 1133 (s), 1068 (w), 979 (s), 799 (m), 734 (w), 718 cm^{-1} (w); Raman (1064 nm): $\tilde{\nu}$ = 3234 (10), 2258 (97), 1680 (4), 1644 (2), 1439 (15), 1410 (4), 1384 (3), 1322 (2), 1208 (3), 1140 (6), 1075 814), 1001 (36), 886 (9), 801 (8), 734 (1), 719 (3), 680 (4), 639 (3), 600 (2), 571 (8), 503 (8), 477 (7), 410 (4), 354 cm^{-1} (3); ^{1}H NMR ([D$_6$]DMSO): δ = 8.58 (br s, 3H, C-NH-NH$_2$), 4.48 ppm (br s, 6H, N-NH_2); ^{13}C NMR ([D$_6$]DMSO): δ = 159.6 (s, 1C, C(NHNH$_2$)$_3$), 131.6 (s, 1C, CN$_4$O), 112.8 ppm (s, 1C, CN); MS (FAB$^-$) m/z: 109.9 (C$_2$N$_5$O); (FAB$^+$) m/z:105.1 (C(NHNH$_2$)$_3$); elemental analysis calcd (%) for CN$_6$H$_9$C$_2$N$_5$O (215.18): C 16.74, N 71.6, H 4.21; found: C 16.72, N 70.77, H 4.19. BAM impact: 40 J; BAM friction: 324 N; ESD: 550 mJ.

Aminoguanidinium cyanotetrazolate-1-oxide (8)

To a solution of aminoguanidinium chloride (102 mg, 0.92 mmol) in 20 mL of distilled water, **3** (200 mg, 0.92 mmol) was added in the dark, and the mixture was shaken for 10 min. After filtration, the filtrate was evaporated to dryness to yield **8** as a white solid (0.16 g, 94%). DSC (5°Cmin^{-1}): 66°C (m.p.), 164°C (dec); IR: $\tilde{\nu}$ = 3467 (w), 3361 (m), 3143 (w), 3060 (w), 2972 (w), 2853 (w), 2643 (w), 2251 (w), 2171 (w), 1655 (vs), 1625 (m), 1463 (m), 1413 (m), 1245 (s), 1221 (m), 1144 (w), 1093 (w), 1007 (w), 973 (w), 889 (w), 772 (m), 682 cm^{-1} (w); Raman (1064 nm): $\tilde{\nu}$ = 3282 (5), 3229 (1), 3197 (1), 3336 (1), 3355 (1), 2490 (1), 2432 (2), 2253 (98), 2198 (2), 1682 (2), 1631 (5), 1564 (2), 1466 (82), 1417 (3), 1387 (2), 1252 (2), 1223 (35), 1145 (18), 1091 (14), 1009 (18), 973 (21), 776 (25), 717 (2), 694 (1), 639 (12), 550 (4), 492 (15), 416 (3), 360 (2), 246 cm^{-1} (1); ^{13}C NMR ([D$_6$]DMSO): δ = 159.4 (s, AG$^+$); 123.9 (s, CN4); 110.9 ppm (s, CN); ^{1}H NMR ([D$_6$]DMSO): δ = 8.58 (s, 1H, NH-NH$_2$); 7.01 (br s, 2H, NH$_2$); 6.99 (s, 2H, NH$_2$); 4.51 ppm (br s, 2H, NH-NH$_2$); m/z (FAB$^+$): 75.1 (CN$_4$H$_7^+$); m/z (FAB$^-$): 110.0 (C$_2$N$_5$O$^-$); elemental analysis calcd (%) for CN$_4$H$_7$C$_2$N$_5$O (185.15): C 19.46, H 3.81, N 68.09; found: C 19.14, H 3.72, N 64.67; BAM impact: 40 J; BAM friction: 216 N; ESD: 0.5 J.

Triaminoguanidinium cyanotetrazolate-1-oxide (9)

In the dark, **3** (250 mg, 1.15 mmol) was added to a solution of triaminoguanidinium chloride (160 mg, 1.15 mmol) in 20 mL of distilled water. The solution was shaken for about 10 min and filtered. The yellow filtrate was evaporated by blowing a N$_2$ flow on the liquid surface to afford **9** as colorless crystals (0.19 g, 77%). DSC (5°Cmin^{-1}): 134°C (m.p.), 150°C (dec); IR: $\tilde{\nu}$ = 3343 (m), 3230 (m), 3095 (w), 3008 (w), 2782 (w), 2659 (w), 2248 (w), 1841 (w), 1674 (vs), 1611 (w), 1590 (w), 1536 (m), 1458 (w), 1418 (m), 1387 (w), 1345 (m), 1246 (s), 1210 (w), 1190 (m), 1131 (s), 1073 (w), 1014 (w), 995 (m), 942 (s), 928 (s), 793 (w), 770 (w), 684 cm^{-1} (w); Raman (1064 nm): $\tilde{\nu}$ = 3345 (4), 3239 (8), 2249 (98), 2194 (2), 1678 (4), 1646 (1), 1459 (47), 1391 (2), 1350 (3), 1248 (2), 1211 (16), 1202 (3); 1138 (9), 1074 (18), 1011 (10), 880 (10), 771 (15), 696 (1), 647 (10), 548 (4), 494 (12), 429 (6), 313 (1), 257 cm^{-1} (4); ^{13}C NMR ([D$_6$]DMSO): δ = 159.6 (s, TAG$^+$); 123.9 (s, CN4); 110.8 ppm (s, CN); ^{1}H NMR ([D$_6$]DMSO): δ = 8.58 (s, 3H, NH-NH$_2$); 4.48 ppm (s, 6H, NH-NH$_2$); MS (FAB$^+$) m/z: 105.1 (CN$_6$H$_9^+$); (FAB$^-$) m/z: 110.0 (C$_2$N$_5$O$^-$); elemental analysis calcd (%) for CN$_6$H$_9$C$_2$N$_5$O (215.18): C 16.75, H 4.22, N 71.60; found: C 16.87, H 4.12, N 70.13; BAM impact: 40 J; BAM friction: 216 N; ESD: 0.5 J.

Copper(II) bis(carboxamide-tetrazolate-2-oxide) dihydrate (10)

To a solution of copper (II) chloride dihydrate (78 mg, 0.46 mmol) in 15 mL of distilled water, finely powdered **1** (200 mg, 0.92 mmol) was added in the dark. The suspension was carefully shaken by hand for 15 min in the dark followed by filtration. The filtrate was evaporated under heating (40°C) to give **10** as green single crystals (89.3 mg, 55%). IR: $\tilde{\nu}$ = 3854 (w), 3752 (w), 3377 (w), 3341 (w), 3270 (w), 3068 (m), 2782 (w), 2362 (w), 2333 (w), 2206 (w), 1734 (w), 1670 (s), 1590 (m), 1522 (m), 1444 (m), 1406 (w), 1387 (m), 1333 (s), 1246 (m), 1150 (w), 1119 (w), 1069 (w), 999 (w), 981 (w), 894 (w), 872 (w), 822 (m), 784 (w), 703 (m), 687 cm^{-1} (m); elemental analysis calcd (%) for Cu(C$_2$N$_5$H$_4$O$_3$)$_2$ (355.65): C 13.51, N 39.38, H, 2.27; found: C 14.08, N 41.28, H 2.2.

Copper(II) bis(carboxamide-tetrazolate-1-oxide) dihydrate (11)

3 (200 mg, 0.92 mmol) was added to a solution of copper(II) chloride dihydrate (78 mg, 0.46 mmol) in 20 mL of distilled water. The solution was shaken for 10 min and filtered in the dark. The light blue filtrate was evaporated under heating (40°C) to yield **11** as green crystals (124 mg, 0.35 mmol). IR: $\tilde{\nu}$ = 3854 (w), 3746 (w), 3651 (w), 3447 (w), 3377 (w), 3298 (w), 3220 (w), 3170 (w), 2361 (m), 2338 (m), 2111 (w), 1734 (w), 1674 (vs), 1653 (s), 1610 (s), 1560 (w), 1530 (m), 1473 (w), 1457 (w), 1435 (w), 1419 (w), 1378 (m), 1338 (w), 1251 (m), 1208 (m), 1118 (w), 1092 (w), 1016 (w), 820 (w), 784 (m), 732 (w), 706 (m), 684 (w), 668 cm^{-1} (w); elemental analysis calcd (%) for CuC$_4$N$_{10}$O$_6$H$_8$ (355.72): C 13.51, H 2.27, N 39.38; found: C 13.78, H 2.23, N 40.63.

Hydrazinium 1,4-bis(2-N-oxidotetrazolate)-dihydro-1,2,4,5-tetrazine (12)

Sodium-5-cyano-tetrazolate·1.5 H$_2$O (5.00 g, 34.7 mmol, 1.0 equiv) was dissolved in 25 mL water. The solution was cooled to 0°C and nitric acid (18.5 mL, 2 M, 37.0 mmol, 1.1 equiv) was added. The mixture was stirred for 30 min before it was allowed to warm up to room temperature. The solvent was then removed under reduced pressure at room temperature and the residue was dissolved in ethanol. Remaining solids were filtered off, and the ethanol was evaporated at room temperature under reduced pressure to yield crude 5-cyanotetrazole. The crude product was dissolved in 66 mL water. Subsequently, 2 M potassium hydroxide (17.5 mL, 35.0 mmol, 1.0 equiv), potassium acetate (29.80 g, 303.6 mmol, 8.7 equiv), and Oxone (66.03 g, 107.4 mmol, 3.1 equiv) were added. The solution was stirred at 40°C overnight. The solution was then poured into acetone (1.60 L) and stirred, followed by filtration of precipitated salts. After evaporation of the acetone under reduced pressure, the remaining solids were dissolved in hot ethanol. The insoluble remains were filtered off, and the ethanol was removed under reduced pressure. The residue was then dissolved in 15 mL water. The solution was cooled to 0°C before 2 M nitric acid (17.4 mL, 34.7 mmol, 1.0 equiv) was added. After stirring the mixture for 30 min, the solvent was evaporated under high vacuum at room temperature. The solid residue was dissolved in dry ethanol, and insoluble remains were filtered off. Next, hydrazine hydrate (2.96 mL,

3.06 g, 60.9 mmol, 1.8 equiv) was added and the mixture was refluxed at about 85 °C for 2 h before additional hydrazine hydrate (2.96 mL, 3.06 g, 60.9 mmol, 1.8 equiv) was added. Subsequently, the mixture was refluxed for another 22 h. The precipitate was filtered off and rinsed with dry ethanol to yield **12** as a white solid (4.38 g, 13.9 mmol, 79.8% relative to the amount of sodium 5-cyanotetrazolate sesquihydrate). DSC: 176 °C (dec.); IR: $\tilde{v}$ = 3306 (w), 3272 (w), 3187 (w), 3148 (w), 3079 (w), 2945 (w), 2877 (w), 2649 (w), 2520 (w), 2151 (w), 2119 (w), 1637 (w), 1613 (w), 1545 (w), 1512 (w), 1461 (w), 1448 (w), 1406 (m), 1396 (m), 1372 (s), 1302 (w), 1246 (m), 1193 (w), 1100 (m), 1038 (w), 1014 (w), 993 (w), 972 (m), 864 (w), 783 (m), 749 (w), 724 (w), 701 (w), 650 cm^{-1} (m); Raman (1064 nm): $\tilde{v}$ = 1662 (95), 1625 (8), 1589 (34), 1544 (46), 1515 (2), 1455 (31), 1414 (2), 1399 (6), 1374 (3), 1301 (2), 1237 (9), 1194 (2), 1119 (26), 1051 (5), 1030 (66), 975 (14), 843 (2), 763 (2), 787 (1), 749 (10), 702 (1), 646 (4), 597 (2), 541 (3), 456 (3), 333 cm^{-1} (3); ^{13}C NMR ([D$_6$]DMSO,): δ = 148.10 (s) 140.54 ppm (s); MS (FAB$^+$): m/z = 33.1 (N$_2$H$_5$$^+$), MS (FAB$^-$, glycerine): m/z = 251.1 (C$_4$H$_3$N$_{12}$O$_2$$^-$); elemental analysis calcd (%) for (N$_2$H$_5$)$_2$C$_4$N$_{12}$O$_2$H$_2$ (316.24): N 70.87, C 15.19, H 3.82; found: N 64.81, C 15.49, H 3.62; BAM impact: 35 J; BAM friction: 360 N; ESD 250 mJ.

Hydrazinium 1,4-bis(1-N-oxidotetrazolate)-dihydro-1,2,4,5-tetrazine (13)

Sodium cyanotetrazolate-1-oxide (2.00 g, 14.1 mmol, 1.0 equiv) was dissolved in 12 mL of water. The solution was then cooled to 0 °C before 2 M nitric acid (7.04 mL, 14.1 mmol, 1.0 equiv) was added. After stirring the mixture for 30 min, the solvent was evaporated under reduced pressure at room temperature. The solid residue was dissolved in dry ethanol, and insoluble remains were filtered off. Subsequently, hydrazine hydrate (1.20 mL, 1.24 g, 24.7 mmol, 1.8 equiv) was added and the mixture was refluxed at 85 °C for 2 h before another portion of hydrazine hydrate (1.20 mL, 1.24 g, 24.7 mmol, 1.8 equiv) was added. The mixture was refluxed for another 22 h. The precipitate was filtered off and rinsed with dry ethanol to yield **13** as a white solid (1.84 g, 82.5%). DSC: 134 °C (m.p.), 180 °C (dec.); IR: $\tilde{v}$ = 3589 (w), 3260 (s), 3183 (m), 3111 (m), 2968 (m), 2909 (m), 2726 (w), 2635 (w), 2298 (w), 2202 (w), 2056 (w), 1988 (w), 1954 (w), 1903 (w), 1653 (m), 1615 (m), 1538 (w), 1514 (s), 1457 (s), 1445 (s), 1411 (m), 1346 (w), 1318 (m), 1243 (s), 1167 (m), 1150 (w), 1103 (s), 1082 (s), 1005 (m), 988 (s), 951 (m), 853 (s), 782 (m), 737 (m), 725 (s), 698 (m), 654 cm^{-1} (w); Raman (1064 nm): $\tilde{v}$ = 3256 (13), 3220 (3), 3002 (3), 2929 (5), 1950 (4), 1907 (3), 1855 (3), 1806 (3), 1770 (3), 1732 (2), 1655 (94), 1594 (43), 1547 (48), 1518 (3), 1473 (28), 1437 (2), 1400 (4), 1354 (4), 1317 (2), 1299 (8), 1277 (2), 1243 (35), 1159 (16), 1143 (2); 1098 (28), 1044 (3), 1014 (16), 989 (2), 974 (4), 845 (16), 760 (6), 736 (11), 698 (5), 634 (7), 599 (3), 542 (4), 432 (7), 408 (2), 377 (3), 331 (3), 281 cm^{-1} (3); ^{1}H NMR ([D$_6$]DMSO): δ = 10.04 (s, N-H), 7.07 ppm (s, N$_2$H$_5$$^+$); ^{13}C NMR ([D$_6$]DMSO,): δ = 140.44 (s), 134.26 ppm (s); MS (FAB$^-$, glycerin): m/z = 251.1 (C$_4$H$_3$N$_{12}$O$_2$$^-$); elemental analysis calcd (%) for (N$_2$H$_5$)$_2$C$_4$N$_{12}$O$_2$H$_2$ (316.24): N 70.87, C 15.19, H 3.82; found: N 65.55, C 15.15, H 3.75; BAM impact: 40 J; BAM friction: >360 N; ESD: 250 mJ.

1,4-Bis(2-hydroxytetrazole)-dihydro-1,2,4,5-tetrazine dihydrate (14·2H$_2$O)

12 (950 mg, 3.0 mmol, 1.0 equiv) was dissolved in as little hot water as possible, and insoluble remains were filtered off. Subsequently, concentrated hydrochloric acid (37 wt.%, 1.9 mL, 2.26 g, 22.9 mmol, 7.6 equiv) was added and the solution was cooled to 6 °C. The precipitating product was isolated by suction filtration and rinsed with cold water to yield **14·2H$_2$O** as a white solid (315 mg, 36.3%). DSC: 116 °C (-H$_2$O), 162 °C (dec.); IR: $\tilde{v}$ = 3528 (w), 3421 (w), 3273 (m), 3191 (m), 3107 (m), 2975 (m), 2889 (m), 2525 (m), 2365 (m), 2119 (w), 1984 (w), 1972 (w), 1956 (w), 1629 (w), 1564 (m), 1547 (63), 1539 (m), 1512 (w), 1453 (w), 1446 (w), 1385 (s), 1366 (s), 1239 (s), 1197 (m), 1152 (m), 1129 (m), 1103 (m), 1041 (m), 1015 (m), 993 (s), 856 (m), 771 (s), 694 cm^{-1} (s); Raman (1064 nm): $\tilde{v}$ = 3285 (3), 1665 (98), 1547 (63), 1456 (41), 1385 (3), 1242 (9), 1137 (13), 1038 (49), 974 (7), 842 (4), 767 (1), 750 (9), 633 (4), 599 (1), 543 (3), 463 (1), 416 (1), 331 cm^{-1} (1); ^{1}H NMR ([D$_6$]DMSO): δ = 8.86 (br s, -NH), 4.40 ppm (br s, -OH and hydration water); ^{13}C NMR ([D$_6$]DMSO,): δ = 150.39 (s), 139.71 ppm (s); MS (FAB$^-$): m/z = 251 (C$_4$H$_3$N$_{12}$O$_2$$^-$); elemental analysis calcd (%) for C$_4$N$_{12}$O$_2$H$_4$·2H$_2$O

(288.18): N 58.32, C 16.67, H 2.80; found: N 63.54, C 16.46, H 3.31; BAM impact: 40 J; BAM friction: 360 N; ESD: 250 mJ.

1,4-Bis(1-hydroxytetrazole)-dihydro-1,2,4,5-tetrazine hydrate (15·H$_2$O)

13 (1.84 g, 5.5 mmol, 1.0 equiv) was dissolved in as little hot water as possible, and insoluble material was filtered off. Subsequently, concentrated hydrochloric acid (37 wt.%, 4 mL, 4.76 g, 48.3 mmol, 8.8 equiv) was added and the solution was cooled to 6 °C. The precipitating product was isolated by suction filtration and rinsed with cold water to yield **15·H$_2$O** as a white solid (0.91 g, 61.1%). DSC: 144 °C (dec.); IR: $\tilde{v}$ = 3556 (w), 3329 (m), 3317 (m), 3234 (m), 3190 (m), 3048 (m), 2952 (w), 2933 (w), 2746 (w), 2651 (w), 2623 (w), 2365 (w), 2337 (w), 2198 (w), 2083 (w), 2048 (w), 1831 (w), 1695 (m), 1641 (m), 1594 (m), 1530 (m), 1469 (w), 1433 (s), 1320 (w), 1308 (w), 1265 (w), 1247 (w), 1230 (w), 1191 (w), 1148 (m), 1138 (m), 1114 (w), 1096 (w), 1062 (w), 1037 (m), 1003 (w), 975 (w), 962 (m), 922 (m), 857 (m), 786 (s), 757 (m), 735 (s), 717 (m), 694 (m), 686 cm^{-1} (m); Raman (1064 nm): $\tilde{v}$ = 3243 (4), 1671 (71), 1646 (15), 1567 (95), 1542 (4), 1464 (9), 1411 (1), 1392 (1), 1286 (4), 1244 (17), 1178 (2), 1138 (8), 1090 (15), 1024 (5), 1005 (1), 973 (1), 863 (8), 790 (3), 727 (12), 693 (12), 640 (4), 536 (3), 384 (3), 319 (3), 234 cm^{-1} (2); ^{1}H NMR ([D$_6$]DMSO): δ = 9.78 (br s, N-H), 4.10 ppm (br s, O-H and H$_2$O); ^{13}C NMR ([D$_6$]DMSO,): δ = 138.70 (s), 136.43 ppm (s); MS (DEI+): m/z = 252.3 (M^+); elemental analysis calcd (%) for C$_4$N$_{12}$O$_2$H$_4$·H$_2$O (270.17): N 62.21, C 17.78, H 2.24; found: N 59.22, C 17.19, H 2.88; BAM impact: 17 J; BAM friction: 192 N; ESD: 700 mJ.

Ammonium 1,4-bis(2-N-oxidotetrazolate)-dihydro-1,2,4,5-tetrazine (16)

14·2H$_2$O (200 mg, 0.79 mmol) was dissolved in 50 mL of distilled water, and then 2 M ammonia (0.8 mL, 1.59 mmol) was added. Subsequently,the solvent was removed under reduced pressure to yield **16** as a solid (185.5 mg, 82%). IR: $\tilde{v}$ = 3262 (w), 3170 (m), 3026 (m), 2853 (m), 2119 (w), 1681 (w), 1604 (w), 1534 (w), 1512 (w), 1430 (m), 1403 (s), 1368 (s), 1274 (w), 1236 (m), 1200 (m), 1154 (w), 1124 (w), 1107 (w), 1048 (w), 1009 (m), 994 (m), 973 (w), 866 (w), 789 (m), 734 (m), 694 cm^{-1} (w); Raman (1064 nm): $\tilde{v}$ = 3264 (3), 3085 (5), 1660 (98), 1536 (64), 1463 (26), 1410 (4), 1395 (1), 1235 (7), 1174 (5), 1122 (37), 1067 (2), 1022 (85), 994 (5), 971 (7), 821 (1), 858 (1), 790 (1), 767 (3), 751 (11), 695 (1), 645 (5), 601 (3), 548 (3), 452 (6), 327 cm^{-1} (4); ^{1}H NMR ([D$_6$]DMSO): δ = 8.3 (s, 2H, C$_2$N$_4$H$_2$), 7.3 ppm (s, 4H, NH$_4$); ^{13}C NMR ([D$_6$]DMSO): δ = 148.6 (s, 2C, -CN$_4$O), 141.1 ppm (s, 2C, -C$_2$N$_4$-); m/z: (FAB$^-$) 251 (C$_4$H$_2$N$_{12}$O$_2$); m/z: (FAB$^+$) 18.1 (NH$_4$); elemental analysis calcd (%) for (NH$_4$)$_2$C$_4$N$_{12}$O$_2$H$_2$ (286.22): C 16.77, N 68.51, H 3.52; found: C 16.37, N 66.96, H 3.73; BAM impact: 30 J; BAM friction: 360 N; ESD: 500 mJ.

Ammonium 1,4-bis(1-N-oxidotetrazolate)-dihydro-1,2,4,5-tetrazine monohydrate (17·H$_2$O)

To a solution of **15·H$_2$O** (0.20 g, 0.79 mmol) in about 4 mL distilled water 2 M ammonia (0.83 mL, 1.66 mmol) was added. After that, the mixture was stirred for 0.5 h and the solvent was evaporated under nitrogen flow to afford **17·H$_2$O** as a white solid (0.22 g, 97%). IR: $\tilde{v}$ = 3314 (w), 3268 (m), 3176 (w), 3040 (w), 2897 (w), 2855 (w), 2734 (w), 2633 (w), 1635 (w), 1549 (w), 1510 (m), 1433 (vs), 1415 (s), 1310 (w), 1282 (m), 1231 (m), 1165 (w), 1133 (w), 1093 (m), 1067 (w), 999 (w), 980 (w), 970 (m), 850 (w), 774 (w), 745 (w), 735 (w), 700 cm^{-1} (w); Raman (1064 nm): $\tilde{v}$ = 3274 (2), 3176 (7), 2131 (2), 1653 (98), 1605 (11), 1536 (49), 1467 (21), 1398 (2), 1357 (1), 1289 (10), 1233 (40), 1148 (12), 1089 (17), 1007 (11), 968 (4), 844 (9), 756 (4), 739 (9), 699 (3), 653 (3), 639 (1), 533 (4), 414 (4), 381 (2), 323 (2), 273 cm^{-1} (1); ^{13}C NMR ([D$_6$]DMSO): δ = 134.8 (s, 2C, -C$_2$N$_4$-); 140.9 ppm (s, 2C, -CN$_4$); ^{1}H NMR ([D$_6$]DMSO): δ = 10.11 (s, 4H, NH$_4$$^+$); 7.11 ppm (br s, 2H, -NH-); m/z (FAB$^+$, NBA): 18.0 (NH$_4$$^+$); m/z (FAB$^-$, NBA): 251.0 (C$_4H_3N_{12}O_2$$^-$); elemental analysis calcd (%) for (NH$_4$)$_2$C$_4$N$_{12}$O$_2$H$_2$·H$_2$O (304.23): C 15.78, H 3.98, N 64.46; found: C 15.80, H 3.96, N 64.54; BAM impact: 40 J; BAM friction: 240 N; ESD: 1.5 J.

1,4-Bis(2-hydroxytetrazole)-1,2,4,5-tetrazine (18)

To a suspension of **14·2H$_2$O** (100 mg, 0.35 mmol, 1.0 equiv) in 100 mL acetonitrile, a solution of nitrogen dioxide in acetonitrile was added

dropwise until the suspension became red and no more of the solid dissolved. The remaining solid was filtered off, and the solution was slowly evaporated under a stream of nitrogen at room temperature. The solid was then dried under high vacuum at 40 °C. WARNING: VERY EXPLOSIVE WHEN DRY! ^{13}C NMR ([D$_6$]DMSO,): $\delta = 158.4$ (s), 154.9 ppm (s); MS (FAB$^-$): $m/z = 249.2$ (C$_4$N$_{12}$O$_2$H$^-$).

Ammonium 1,4,-bis(2-N-oxidotetrazolate)-1,2,4,5-tetrazine monohydrate (20·H$_2$O)

To a suspension of **14·2H$_2$O** (100 mg, 0.35 mmol, 1.0 equiv) in 100 mL acetonitrile, a solution of nitrogen dioxide in acetonitrile was added dropwise until the suspension became red and no more of the solid dissolved. The remaining solid was filtered off, and the solution was slowly evaporated under a stream of nitrogen at room temperature. The obtained product was dissolved in water, and then 2 M ammonia (0.37 mL, 0.74 mmol) was added. Afterwards, the solution was evaporated under a stream of nitrogen to yield **20·H$_2$O** (70 mg, 0.23 mmol) as a red solid after drying under high vacuum. DSC: 95 °C (-H$_2$O), 189 °C (dec.); IR: $\tilde{v} = 3401$ (w), 3165 (m), 3010 (m), 2821 (m), 2361 (w), 2258 (w), 2135 (w), 1831 (w), 1675 (w), 1604 (w), 1570 (w), 1534 (m), 1406 (s), 1354 (s), 1313 (s), 1273 (m), 1263 (m), 1248 (s), 1209 (m), 1098 (w), 1068 (m), 1044 (w), 1011 (m), 992 (m), 921 (w), 825 (w), 787 (m), 781 (m), 742 (w), 703 (w), 676 cm^{-1} (w); Raman (1064 nm): $\tilde{v} = 1997$ (1), 1864 (2), 1628 (1), 1516 (100), 1495 (2), 1425 (7), 1391 (3), 1232 (1), 1152 (2), 1100 (29), 1088 (4), 1036 (3), 1002 (17), 988 (5), 820 (4), 764 (1), 601 (1), 465 cm^{-1} (2); ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.29$ (br s, NH$_4{}^+$), 3.4 ppm (br s, H$_2$O); ^{13}C NMR ([D$_6$]DMSO): $\delta = 158.15$ (s), 150.92 ppm (s); MS (FAB$^-$): $m/z = 249.1$ (C$_4$N$_{12}$O$_2$H$^-$); elemental analysis calcd (%) for (NH$_4$)$_2$C$_4$N$_{12}$O$_2$·H$_2$O (302.22): N 64.89, C 15.89, H 3.34; found: N 59.69, C 16.03, H 3.45; BAM impact: 40 J; BAM friction: 240 N; ESD: 500 mJ;

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