



The Reactivity of 5-Cyanotetrazole towards Water and Hydroxylamine

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Sodium 5-cyanotetrazolate sesquihydrate (**1**) was prepared from sodium azide and two equivalents of sodium cyanide under acidic conditions. Its hydrolysis, when treated with an excess of 6 M nitric acid yields tetrazole-5-carboxamide (**4**), whereas stoichiometric amounts of 2 M nitric acid yields the free acid 5-cyanotetrazole (**2**). 5-Cyanotetrazole readily reacts with hydroxylammonium chloride to form the oxime of tetrazole-5-carboxamide (**6**). Both compounds, the tetrazole-5-carboxamide (**4**) and its oxime (**6**), bear an acidic proton, which can be abstracted with bases such as aqueous ammonia or hydroxylamine, to form the respective hydroxylammonium (**5**, **7**) or ammonium salts (**8**). Also the guanidinium (**9**) and the triaminoguanidinium salt (**10**) were prepared using guanidinium

and triaminoguanidinium chloride, respectively. All mentioned compounds, including the silver salt of 5-cyanotetrazole (**3**), were structurally characterized by low-temperature single-crystal X-ray analysis. In addition, the materials were characterized using NMR and vibrational (IR, Raman) spectroscopy as well as mass spectrometry and elemental analysis. The thermal behavior was studied from DSC measurements and the sensitivities of the compounds towards shock, friction, and electrostatic discharge were determined. Moreover, the heats of formation were calculated (atomization method, CBS-4M enthalpies) and several detonation/propulsion parameters computed with the EXPLO5 code.

Introduction

Since their discovery, the spectrum of different applications of tetrazoles has extended over a very large field during the last century and especially in the last decades, reaching from pharmaceutical compounds^[1] up to energetic materials,^[2] where they are used because of their high nitrogen content and comparatively high thermal stability, which traces back to their stable 6 π -aromatic system. Their preparation utilizes the 1,3-dipolar cycloaddition of inorganic,^[3] organic,^[4,5] silyl,^[6] and complexed metal azides^[7] with nitriles, whereas electron withdrawing groups attached to the nitrile enhance their reactivity towards 1,3-dipoles such as the azide moiety.^[3] This might be a probable reason for the early discovery of 5-cyanotetrazole from a dipolar cycloaddition of cyanogen, which has a very electron-poor environment, with hydrazoic acid generated in situ.^[8] Although the first synthetic route is accomplished in aqueous media, also the preparation employing SO₂ (l) as the solvent was reported recently.^[9] Because the nitrile group in 5-cyanotetrazole is a versatile electrophilic moiety, which additional to its hydrolysis also can react with a variety of different nucleophiles, 5-cyanotetrazole can be regarded as an intermediate in variable syntheses for future applications, which do not only include the above-mentioned sectors of pharmaceutical compounds and energetic materials. Here, the product of the reaction of 5-cyanotetrazole and hydroxylamine, namely tetrazole-5-carboxamide oxime, is introduced and characterized as an example of a transformation of the nitrile moiety into a further useful intermediate for organic synthesis. Polanc and co-workers^[10] report on the use of carboxamide oximes as precursors for the synthesis of pyrimidine N-oxides, while pointing out the use of N-oxides as intermediates or auxiliary

agents in the synthesis, as protecting groups, oxidants, ligands in metal complexes, as catalysts, pharmaceuticals, and agrochemicals.^[10]

Along with the hydrolysis product of 5-cyanotetrazole, tetrazole-5-carboxamide, herein we want to concentrate on the energetic character of tetrazole-5-carboxamide oxime and the nitrogen-rich salts thereof, the synthesis and analytical characterization of which we report in the following.

Results and Discussion

Synthesis

The sodium salt of 5-cyanotetrazole, which has been known since the early 20th century,^[8] is here prepared from a slightly modified procedure in a 2,3-dipolar cycloaddition (Huisgen reaction), starting from sodium azide and two equivalents of sodium cyanide under acidic conditions, using Cu²⁺ as a catalyst and MnO₂ as the oxidizing agent. Here, the cyanide anion is oxidized to cyanogen by Cu²⁺, which is reoxidized by MnO₂ afterwards as depicted in Scheme 1.

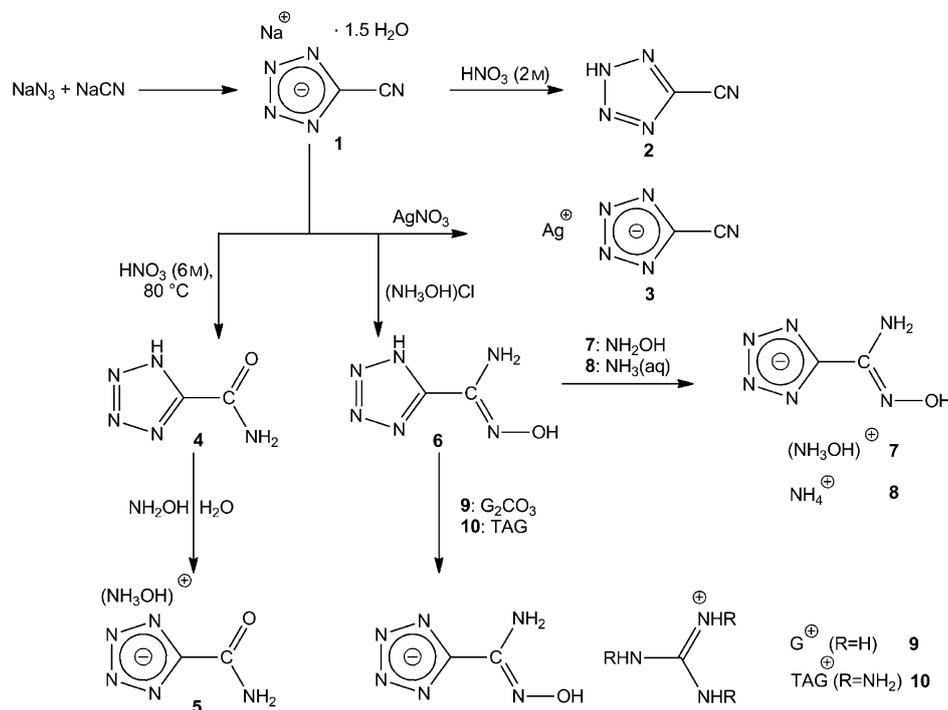
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Scheme 1. Generation of cyanogen in situ.

The cyanogen generated in situ cyclizes with hydrazoic acid to 5-cyanotetrazole. To remove remaining MnO_2 , the reaction mixture is filtrated and the filtrate is treated with Na_2CO_3 to remove Mn^{2+} as its poorly soluble carbonate by filtration and to obtain the sodium salt of 5-cyanotetrazole, which can be extracted with boiling acetone and recrystallized from ethanol/ethyl acetate (2:1; Scheme 2).



Scheme 2. Synthesis of sodium 5-cyanotetrazolate (1), the free acid 2 and the silver salt 3 as well as the tetrazole-5-carboxamide (4), its salt 5 and the tetrazole-5-carboxamide oxime (6), and the salts 7–10 thereof.

The treatment of sodium 5-cyanotetrazolate with different concentrations of nitric acid, such as 2 M and 6 M HNO_3 , yields two different reaction products, which first is the free acid 5-cyanotetrazole (2) in the case of 2 M HNO_3 and second the hydrolysis product tetrazole-5-carboxamide (4) in the case of using 6 M HNO_3 at elevated temperature. Silver 5-cyanotetrazolate (3) can be isolated after combining a silver nitrate solution with a solution of 1. It precipitates instantly owing to its very low water solubility, but nevertheless, it was possible to obtain single crystals of 3 from slowly cooling down a hot solution of 3 in *N,N'*-dimethylformamide (DMF). Silver salt 3 is a primary explosive with high sensitivities towards shock, friction, and electrostatic discharge!

The electrophilic reactivity of nitriles can be used in reactions with hydroxylamine leading to the respective carboxamide oxime.^[11] Based on 5-cyanotetrazole, tetrazole-5-carboxamide oxime (6) can be isolated in yields up to 70%. Alternatively, hydroxylammonium chloride and 1, instead of hydroxylamine and 2, can be used. Here, the hydroxylammonium cation is partially deprotonated in the reaction mixture by the tetrazole moiety, resulting in a higher nucleophilicity of the amine moiety, which is necessary for the reaction with the cyano group of 1. Tetrazole-5-carboxamide oxime (6) again can be deprotonated at the tetrazole ring using nitrogen-rich bases such as hydroxylamine, ammonia, guanidinium carbonate, or triaminoguanidine, resulting in the respective salts hydroxylammonium tetrazole-5-carboxamide oxime (7), ammonium tetrazole-5-carboxamide oxime (8), guanidinium tetrazole-5-carboxamide oxime (9), and 1,3,5-triaminoguanidinium tetrazole-5-carboxamide oxime (10), respectively. Beside 7, also the hydroxylammonium salt of tetrazole-5-carboxamide was isolated after deprotonation of 4 in aqueous solution. Single crystals of all described compounds, except for the tetrazole-5-carboxamide oxime (6), the corresponding free acid could be obtained after recrystallization from ethanol/ethyl acetate (2:1; 1), ethanol (2), *N,N'*-dimethylformamide (3), water (4), or ethanol/water (ca. 10:1 to 20:1; 5, 7–10), respectively.

Crystal structures

The crystal structures of compounds 2–5 as well as 7–10 were determined by low-temperature X-ray analysis. Different parameters regarding the measurements and solutions are gathered in Table 1 and Table 2. Although the crystal structure of

ammonium, sodium, potassium, and guanidinium salt were described,^[9] the structure of the parent compound is still unknown. 5-Cyanotetrazole (2) crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the unit cell. Its density of 1.635 g cm^{-3} is in agreement to other neutral tetrazole compounds reported in the literature, for example, 5-oxotetrazole (1.699 g cm^{-3}).^[12] The proton connected to the ring nitrogen atom N2 participates in two hydrogen bonds forming a planar structure shown in Figure 1.

The highly sensitive silver salt 3 crystallizes in the monoclinic space group $P2_1/n$ with a density of 3.245 g cm^{-3} , which is slightly higher than that of silver 1-methyl-5-nitriminotetrazolate (2.948 g cm^{-3}).^[13] The coordination sphere of the silver

Table 1. X-ray diffraction data and parameters.

	2	3	4	5	7	8	9	10
formula	C ₂ H ₅ N ₅	C ₂ AgN ₅	C ₃ H ₃ N ₅ O	C ₅ H ₉ N ₆ O ₂	C ₂ H ₃ N ₅ O ₂	C ₃ H ₃ N ₅ O	C ₃ H ₃ N ₅ O	C ₃ H ₃ N ₅ O
<i>M_r</i> [g mol ⁻¹]	95.08	201.94	113.09	146.13	161.15	145.15	187.19	232.25
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> ₂ ₁ / <i>m</i>	<i>P</i> ₂ ₁ / <i>n</i>	<i>P</i> ₂ ₁ / <i>m</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>n</i>	<i>C</i> ₂ / <i>c</i>	<i>Pca</i> ₂	<i>P</i> ₂ ₁ / <i>n</i>
color/habit	colorless platelet	colorless block	colorless platelet	colorless block	colorless block	colorless block	colorless rod	colorless block
size [mm]	0.04×0.22×0.27	0.10×0.14×0.21	0.10×0.23×0.30	0.18×0.20×0.21	0.18×0.19×0.28	0.18×0.18×0.20	0.10×0.10×0.20	0.20×0.22×0.28
<i>a</i> [Å]	5.085(3)	6.8789(4)	4.9867(3)	10.5123(9)	3.6131(4)	25.578(3)	1.27861(9)	8.5050(11)
<i>b</i> [Å]	6.103(2)	7.6299(5)	6.1274(4)	8.3076(5)	13.1996(17)	3.6503(4)	8.6469(5)	7.1498(12)
<i>c</i> [Å]	6.294(2)	7.9473(4)	7.2221(4)	6.8496(6)	13.4657(14)	13.4265(15)	7.4790(5)	16.028(2)
α [°]	90	90	90	90	90	90	90	90
β [°]	98.54(4)	97.657(5)	100.421(5)	102.185(8)	93.827(11)	103.357(12)	90	101.821(14)
γ [°]	90	90	90	90	90	90	90	90
<i>V</i> [Å ³]	193.16(15)	413.40(4)	217.04(2)	584.71(8)	640.77(13)	1219.7(2)	826.88(9)	954.0(2)
<i>Z</i>	2	4	2	4	4	8	4	4
ρ_{calc} [g cm ⁻³]	1.635	3.245	1.730	1.660	1.670	1.581	1.504	1.617
μ [mm ⁻¹]	0.126	4.723	0.143	0.143	0.143	0.129	0.120	0.130
<i>F</i> (000)	96	376	116	304	336	608	392	488
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	173	173	173	173	173	173	173	173
θ min, max [°]	4.7, 27.5	4.2, 26.0	4.2, 28.2	4.7, 26.5	4.3, 25.0	4.9, 26.0	4.2, 26.7	4.1, 26.4
dataset	-6.6; -7.5; -8.8	-8.8; -8.9; -9.6	-6.6; -7.8; -9.7	-13.13; -10.10; -8.8	-4.4; -15.10; -15.15	-18.30; -4.4; -16.16	-14.16; -10.10; -9.7	-10.10; -8.8; -20.10
reflections collected	1121	1449	1321	5947	2981	2965	4298	4877
independent reflections	487	810	580	1210	1122	1204	949	1934
<i>R</i> _{int}	0.058	0.025	0.033	0.056	0.039	0.042	0.036	0.044
observed reflections	376	639	415	762	782	886	861	1445
parameters	47	73	58	115	100	119	154	193
<i>R</i> ₁ (obs)	0.0537	0.0263	0.0324	0.0322	0.0419	0.0391	0.0287	0.0412
<i>wR</i> ₂ (all data)	0.1438	0.0505	0.0841	0.0626	0.1037	0.0882	0.0673	0.1029
<i>S</i> ^a	1.13	0.92	0.94	0.80	0.93	1.01	1.08	1.07
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e Å ⁻³]	-0.26, 0.31	-0.66, 0.58	-0.19, 0.24	-0.16, 0.25	-0.24, 0.37	-0.21, 0.22	-0.16, 0.16	-0.25, 0.22
device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
solution	SIR-92	SIR-92	SHELXS-97	SIR-92	SIR-92	SIR-92	SHELXS-97	SIR-92
refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
absorption correction	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan
CCDC	867191	867194	867192	867195	867196	867198	867199	867197

Table 2. CBS-4M calculation results, molecular volumes taken from X-ray measurements, and calculated lattice enthalpy.

M	$-H^{298}$ [a.u.]	$\Delta_f H^\circ(\text{g}, \text{M})$ [kJ mol $^{-1}$]	V_M [nm 3]	ΔH_L [kJ mol $^{-1}$]
5 anion	425.907415	58.4	—	—
6 anion	481.115424	148.0	—	—
NH $_4^+$	56.796608	635.8	—	—
NH $_4\text{O}^+$	131.863249	687.2	—	—
G $^+$	205.453192	571.9	—	—
TAG $^+$	371.197775	874.3	—	—
5	—	628.8	0.146	554.1
7	—	835.2	0.160	540.7
8	—	783.8	0.152	547.9
9	—	719.9	0.207	505.5
10	—	1022.3	0.239	487.1

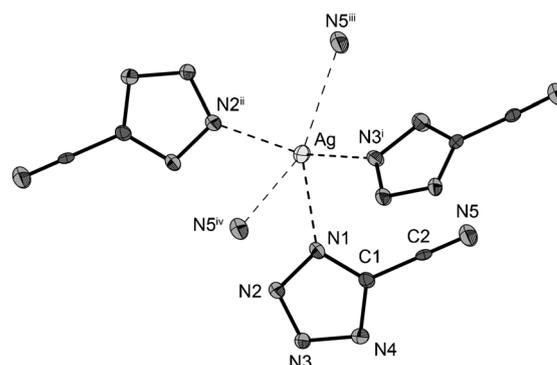


Figure 2. Coordination of the Ag $^+$ cation in the structure of **3**. Thermal ellipsoids represent the 50% probability level. Selected coordination distances [Å]: Ag–N1 2.408(4), Ag–N3 i 2.260(5), Ag–N2 ii 2.242(4), Ag–N5 iii 2.750(4), Ag–N5 iv 2.951(6); symmetry codes: i) 0.5 + x, 0.5 – y, 0.5 + z; ii) 1 – x, – y, 1 – z; iii) 1 – x, – y, 2 – z; iv) 0.5 + x, 0.5 – y, – 0.5 + z.

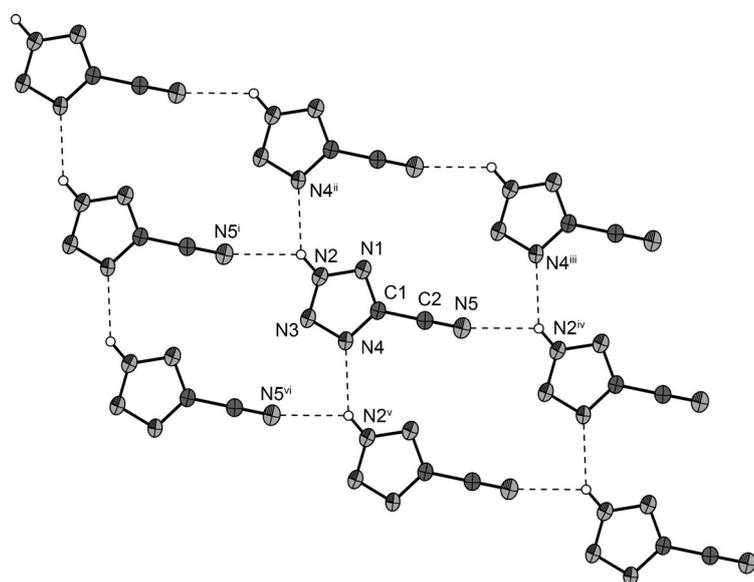


Figure 1. Hydrogen bonding in the structure of **2**. Thermal ellipsoids represent the 50% probability level. Selected bond lengths [Å]: N4–N3 1.318(3), N4–C1 1.339(4), N3–N2 1.318(3), N2–N1 1.311(3), N1–C1 1.328(4), N5–C2 1.138(4), C1–C2 1.438(4); selected bond angles [°]: N3–N4–C1 105.6(2), N2–N3–N4 105.6(2), N1–N2–N3 115.0(2), N2–N1–C1 100.7(2), N1–C1–N4 113.2(3), N1–C1–C2 122.0(3), N4–C1–C2 124.8(2), N5–C2–C1 179.5(3); hydrogen bonds [D–H...A, d(H...A), d(D...A), <(D–H...A)]: N2–H2...N5 i 0.87(4) Å, 2.30(4) Å, 2.948(4) Å, 131(3)°; N2–H2...N4 ii 0.87(4) Å, 2.27(4) Å, 3.001(4) Å, 142(4)°; symmetry codes: i) –1 + x, y, –1 + z; ii) –1 + x, y, z; iii) x, y, 1 + z; iv) 1 + x, y, 1 + z; v) 1 + x, y, z; vi) x, y, –1 + z.

atoms (< 3 Å) is shown in Figure 2. The found coordination number of five is typical for strongly ionic silver complexes caused by hard ligands. The shortest contacts are Ag–N3 i 2.260(5) Å and Ag–N2 ii 2.242(4) Å with an angle of N3 i –Ag–N2 ii of 51.8(1)°. The molecular structure of the cation is in agreement to other cyanotetrazolates in the literature.^[9] The tetrazole/ate rings in all structures are planar with bond distances between typical C–N/N–N and C=N/N=N bonds owing to their aromaticity. The cyano bond length C2–N5 of 1.134(5) Å corresponds to an elongated C=N bond, while the C1–C2 length of 1.452(5) Å is significantly shorter than a C–C bond (1.54 Å).

1H-Tetrazole-5-carboxamide (**4**) crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the unit cell. The density of 1.730 g cm $^{-3}$ is comparable to that observed for 5-azidotetrazole (1.72 g cm $^{-3}$).^[14] The ring proton is now connected to the nitrogen atom N1. The three acidic protons form an intense hydrogen-bond network shown in Figure 3. The corresponding N1-methylated product has been structurally characterized in the literature,^[15] showing a significantly lower density of 1.457 g cm $^{-3}$. Its molecular structure is in agreement to that of compound **4**.

Hydroxylammonium 5-carboxamido-tetrazolate (**5**), crystallizing in the monoclinic space group $P2_1/c$, has a lower density (1.66 g cm $^{-3}$) in comparison to its neutral parent compound **4**. The structure of the anion, shown in Figure 4, is in agreement to the corresponding potassium salt,^[15] which is the only ionic structure of **4** that has been structurally characterized in literature so far. All hydrogen atoms of the hydroxylammonium cation participate in hydrogen bonds to form a 3-dim network.

The structural motif of deprotonated **6**, shown in Figure 5, has never been described in the literature before. Unfortunately, we were not able to obtain single crystals of the parent compound **6**. The investigated salts **7–10** all crystallize in common space groups (**7, 10**: $P2_1/n^{-1}$, **8**: $C2/c^{-1}$, **9**: $Pca2_1$) with different densities (**7**: 1.670, **8**: 1.581, **9**: 1.504, **10**: 1.617 g cm $^{-3}$). The structures of the anions are similar with respect to their bond lengths (and angles) and are given in the captions of Figures 5–8. In all cases the atoms C1, C2, N1, N2, N3, and N4 lie within a plane. The amine and hydroxyimine groups are slightly twisted out of the ring plane with torsion angles N1–C1–C2–N5 of 21.3° (**7**), 33.3° (**8**), 11.6° (**9**), and 15.2° (**10**).

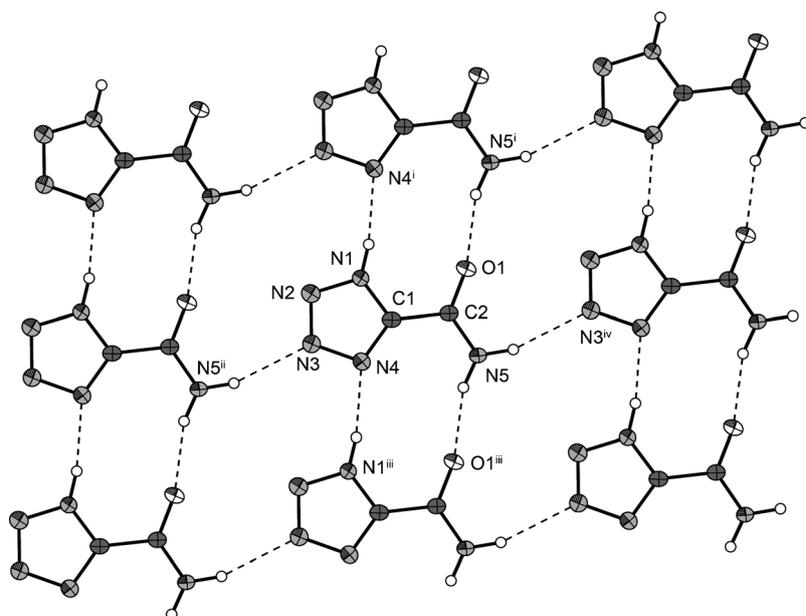


Figure 3. Hydrogen bonding in the structure of 1*H*-tetrazole-5-carboxamide (**4**). Thermal ellipsoids represent the 50% probability level. Selected bond lengths [Å]: N1–C1 1.334(2), N1–N2 1.337(2), N5–C2 1.322(2), O1–C2 1.2306(19), N4–C1 1.324(2), N4–N3 1.365(2), N2–N3 1.298(2), C2–C1 1.488(2); selected bond angles [°]: C1–N1–N2 109.35(14), C1–N4–N3 105.64(13), N3–N2–N1 106.27(14), N2–N3–N4 110.57(13), O1–C2–N5 124.70(15), O1–C2–C1 117.39(14), N5–C2–C1 117.92(14), N4–C1–N1 108.18(15), N4–C1–C2 131.67(15), N1–C1–C2 120.15(14); hydrogen bonds [D–H...A, d(D–H), d(H...A), d(D...A), <(D–H...A)]: N1–H1...N4ⁱ 0.90(3) Å, 1.96(3) Å, 2.845(2) Å, 171(3)°; N5–H51...O1ⁱⁱⁱ 0.91(3) Å, 1.92(3) Å, 2.804(2) Å, 163(2)°, N5–H52...N3^{iv} 0.92(2) Å, 2.24(2) Å, 3.121(2) Å, 162.4(18)°; symmetry codes: i) $-1+x, y, z$; ii) $x, y, -1+z$; iii) $1+x, y, z$; iv) $x, y, 1+z$.

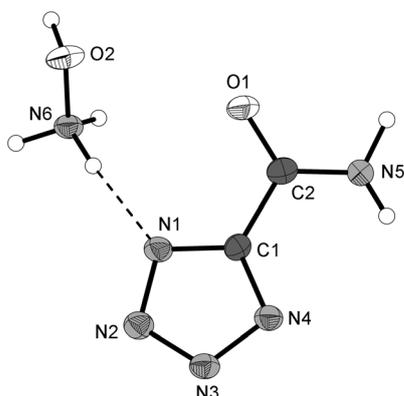


Figure 4. Molecular unit of hydroxylammonium 5-carboxamido-tetrazolate (**5**). Ellipsoids of nonhydrogen atoms are drawn at the 50% probability level. Selected bond lengths (Å): C1–N4 1.3316(18), C1–N1 1.333(2), C1–C2 1.486(2), N4–N3 1.3404(18), N3–N2 1.3218(17), N2–N1 1.3365(17), N5–C2 1.308(2), C2–O1 1.2481(18), O2–N6 1.4103(17); selected bond angles (°): N4–C1–N1 112.61(16), N4–C1–C2 126.54(16), N1–C1–C2 120.82(14), C1–N4–N3 103.73(14), N2–N3–N4 110.13(12), N3–N2–N1 108.95(12), C1–N1–N2 104.58(12), O1–C2–N5 122.91(17), O1–C2–C1 118.07(16), N5–C2–C1 119.03(15).

NMR spectroscopy

All compounds **1–10** were investigated using ^1H and ^{13}C NMR spectroscopy. The chemical shifts are related to tetramethylsilane as standard. Here, an interesting comparison between the spectra of 5-cyanotetrazole and its hydrolysis products tetrazole-5-carboxamide and tetrazole-5-carboxamide oxime seems appropriate.

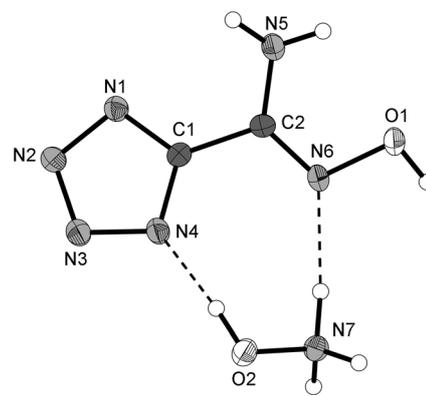


Figure 5. Molecular unit of hydroxylammonium 5-(*N*-hydroxy-carboximidamide)-tetrazolate (**7**). Thermal ellipsoids represent the 50% probability level. Selected bond lengths [Å]: O1–N6 1.414(2), N1–C1 1.331(3), N1–N2 1.346(3), N2–N3 1.313(3), N3–N4 1.341(2), N4–C1 1.330(3), N5–C2 1.347(3), N6–C2 1.285(3), C1–C2 1.474(3), O2–N7 1.416(2).

sis (**4**: $\delta = 152.0$ ppm, **6**: $\delta = 150.7$ ppm). The same applies also to the nitrile carbon atom, which is shifted from $\delta = 112.3$ ppm in **2** to 157.2 ppm in **4**, and 144.9 ppm in **6**.

The hydroxylammonium salt of **4** (**5**), in addition to the amide proton signals, reveals the signal of the protons of the hydroxylammonium cation at $\delta = 10.06$ ppm in the proton NMR spectrum and slightly changed chemical shifts for the carbon atoms as compared to **4** in its ^{13}C NMR spectrum. Both signals are shifted downfield to $\delta = 163.1$ and 157.4 ppm, respectively.

The proton NMR spectrum of **2** shows one singlet at 13.02 ppm, that can be assigned to the relatively acidic proton at the tetrazole ring, which is slightly shifted upfield in the spectrum of the less acidic compound **6** ($\delta = 10.51$ ppm). In addition, the comparatively sharp signal of the oxime proton is visible at $\delta = 7.09$ ppm, whereas the amino group can only be assigned to a broad elevation of the baseline at around $\delta = 6.30$ ppm. The hydrolysis product **4** reveals two distinct singlets in its proton NMR spectrum, which can be assigned to the amino protons of the amide functionality at $\delta = 8.57$ and 8.19 ppm, which show hindered rotation owing to the amide resonance.

The tetrazole carbon atom of **2** is visible as a signal at $\delta = 139.3$ ppm, which is strongly shifted downfield upon hydroly-

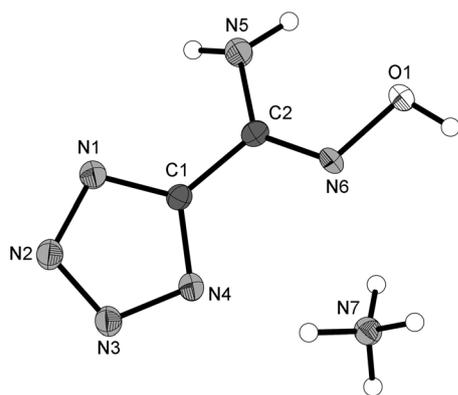


Figure 6. Molecular unit of ammonium 5-(*N*-hydroxy-carboximidamide)-tetrazolate (**8**). Thermal ellipsoids represent the 50% probability level. Selected bond lengths [Å]: O1–N6 1.421(2), N1–C1 1.336(2), N1–N2 1.352(2), N2–N3 1.323(2), N3–N4 1.345(2), N4–C1 1.344(2), N5–C2 1.362(2), N6–C2 1.290(2), C1–C2 1.474(3).

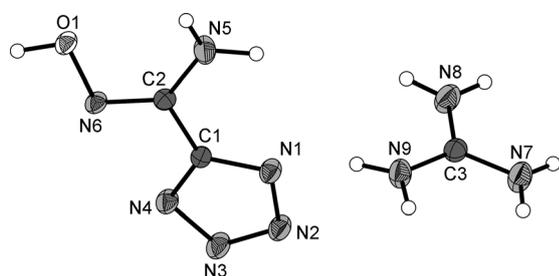


Figure 7. Molecular unit of Guanidinium 5-(*N*-hydroxy-carboximidamide)-tetrazolate (**9**). Thermal ellipsoids represent the 50% probability level. Selected bond lengths [Å]: O1–N6 1.431(2), N1–C1 1.333(3), N1–N2 1.358(3), N2–N3 1.317(3), N3–N4 1.346(3), N4–C1 1.343(3), N5–C2 1.341(3), N6–C2 1.293(3), C1–C2 1.473(3), N7–C3 1.326(3), N8–C3 1.326(3), N9–C3 1.318(3).

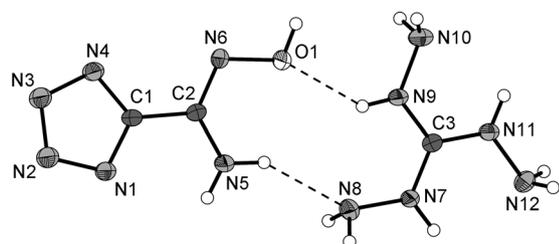


Figure 8. Molecular unit of 1,3,5-triaminoguanidinium 5-(*N*-hydroxy-carboximidamide)-tetrazolate (**10**). Thermal ellipsoids represent the 50% probability level. Selected bond lengths [Å]: O1–N6 1.4345(18), N8–N7 1.417(2), N7–C3 1.322(2), N10–N9 1.406(2), N11–C3 1.322(2), N11–N12 1.406(2), N2–N3 1.318(2), N2–N1 1.345(2), N6–C2 1.294(2), N5–C2 1.343(2), N3–N4 1.353(2), N4–C1 1.337(2), N1–C1 1.334(2), N9–C3 1.332(2), C2–C1 1.474(2).

The proton NMR spectrum of the hydroxylammonium salt of **6** (**7**) shows two broad signals at $\delta=12.31$ and 8.47 ppm, which can be assigned to the hydroxylammonium protons and the protons of the carboxamide-oxime functionality, whereas a definite assignment is not possible. For the ammonium salt **8**, three broad singlets at $\delta=7.35$, 5.59, and 3.49 ppm are observed, which belong to the oxime-OH, NH_2 , and the ammonium cation, respectively. The spectrum of the guanidinium salt

9, in addition to a broad singlet at $\delta=6.61$ ppm (NH_2/OH), shows the guanidinium cation protons in a sharp singlet at $\delta=5.72$ ppm, whereas the proton NMR spectrum of the triaminoguanidinium salt shows a set of four singlets at $\delta=9.44$ (OH), 8.67 (NH, 1,2,3-triaminoguanidinium), 5.51 (NH_2), and 4.54 ppm (NH_2 , 1,2,3-triaminoguanidinium).

Also the carbon atom signals of the anion of the aforementioned salts are slightly shifted downfield upon deprotonation compared to the neutral compound **6** as already observed for **4**. Signals at $\delta=146.5$ – 148.2 ppm are observed for the carbon atom of the carboxamide-oxime moiety and signals at $\delta=156.2$ – 156.5 ppm for the tetrazole carbon atom. The carbon atoms of the guanidinium and triaminoguanidinium cation are visible as signals at $\delta=158.7$ and 159.6 ppm, respectively.

Vibrational spectroscopy

Additional to NMR spectroscopy, IR, and Raman spectroscopy were used for the identification of structural elements and functional groups. Absorptions were assigned according to values reported in the literature and exemplarily discussed for selected compounds in the following.^[16,17] The characteristic vibrations of the tetrazole ring system can be observed in all IR/Raman spectra of **1**–**10**. The tetrazole framework vibrations at $\nu=1001$ – 1209 cm^{-1} , the asymmetric and symmetric stretching vibrations of the N1–C1–N4 fragment^[18] in the range from $\nu=1372$ – 1394 cm^{-1} and the stretching vibration of the cyclic C=N bond are observed. Latter occurs in the same region as the C=N stretching vibration of the oxime subunit and the in-plane scissoring absorption of the NH_2 group **6**–**10**. The mentioned C=N and N–H vibrations appear in a range from $\nu=1542$ – 1712 cm^{-1} , which complicates a clear assignment without quantum chemical calculations. As the IR spectrum of **2** shows a medium absorption at $\nu=1686$ cm^{-1} , which can be definitely assigned to the cyclic C=N bond, it is to assume, that the corresponding absorption bands at $\nu=1682$ cm^{-1} in **6** and $\nu=1712$ cm^{-1} in **8** correspond to the cyclic C=N stretching vibration as well. Because most oximes reported in the literature show weak IR and strong Raman absorptions in the range of $\nu=1620$ – 1690 cm^{-1} ,^[16] it is suggested, that the absorptions at $\nu=1650$ cm^{-1} in the spectrum of **6** and at $\nu=1643$ cm^{-1} in the spectrum of **8** are caused by the exocyclic C=N vibration of the oxime subunit. This finding corresponds with a strong Raman absorption at $\nu=1665$ cm^{-1} , which is found for carboxamide oxime **6**. Thus the remaining absorptions at $\nu=1559$ cm^{-1} (**6**) and $\nu=1542$ cm^{-1} (**8**), can be assigned to in-plane scissoring motions of the NH_2 group. Further characteristic NH_2 bands occur in the range of $\nu=638$ – 856 cm^{-1} and result by out-of-plane wagging motions, which can be identified without doubts in the spectra of **6**–**10**. The nitrile functionality in the Raman and IR spectra of **1** and **2** can be clearly identified as strong absorptions at $\nu=2260$ cm^{-1} (**1**) and $\nu=2280$ cm^{-1} (**2**). Furthermore, N–H and O–H valence vibrations can be observed in the region of $\nu=2744$ – 3461 cm^{-1} . In case of **8**, two well defined sharp absorptions corresponding to asymmetric and symmetric N–H stretching vibrations of the primary amino group appear at $\nu=3454$ cm^{-1} and $\nu=$

3366 cm^{-1} . In the spectrum of **6**, dominating crystal water absorptions avoided such a well-defined separation of the absorption bands. The IR/Raman spectra of tetrazole-5-carboxamide (**4**) and its hydroxylammonium salt **5** nicely show the C=O stretching vibration of the amide moiety in an absorption band at $\nu=1671\text{ cm}^{-1}$ (**5**) and $\nu=1688\text{ cm}^{-1}$ (**4**). Also the N–H stretching modes are visible as absorption bands at $\nu=3250\text{ cm}^{-1}$ in the Raman spectrum of **4** and at $\nu=3201\text{ cm}^{-1}$ in the IR spectrum of **5**.

Sensitivities and thermal stability

The impact sensitivity tests were carried out according to STANAG 4489^[19] modified instruction,^[20] using a BAM (Bundesanstalt für Materialforschung) drop hammer.^[21] The friction sensitivity tests were carried out according to STANAG 4487^[22] modified instruction,^[23] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods" (Impact: Insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a. > 80 N, very sensitive ≤ 80 N, extreme sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.). Compounds **1**, **3**, and **5–10** were also tested upon the sensitivity towards electrical discharge,^[24] using the Electric Spark Tester ESD 2010 EN.^[25] The starting material sodium 5-cyanotetrazolate shows no impact sensitivity (> 40 J), however, it was tested positive in the friction tester (160 N, sensitive). This could be a reason of the inclusion of 1.5 equivalents of crystal water. On the other hand, its silver salt **3** is highly sensitive towards both, impact (< 1 J) and friction (< 5 N).

Tetrazole-5-carboxamide oxime as well as its ammonium and guanidinium salt can be classified as less sensitive towards impact (40 J), whereas the hydroxylammonium (**7**) and the triaminoguanidinium salt (**10**) are more sensitive towards impact (**7**: 10 J, **10**: 15 J), which is a trend, that already has been observed for other nitrogen-rich salts of tetrazole derivatives.^[26] Looking at their friction sensitivity, no definite trend can be observed, however **7**, **9**, and **10** can be classified as less sensitive towards friction (360 N), **6** and **8** need to be classified as sensitive (**6**: 252 N, **8**: 288 N). Also the hydroxylammonium salt of tetrazole-5-carboxamide is less sensitive towards impact (40 J) and shows no enhanced friction sensitivity (288 N), which leads to the assumption, that also tetrazole-5-carboxamide is only less sensitive towards impact and friction, however, these sensitivities have not been tested yet. Also the sensitivities of neutral 5-cyanotetrazole have only be roughly determined. Owing to its electron deficiency in the tetrazole ring it must be also categorized as at least sensitive towards both, impact and friction.

The values for the sensitivities towards electrostatic discharge are spread over a large range from 1 mJ (**3**) to 1 J (**9**, **10**). Not surprisingly, the silver salt of 5-cyanotetrazole shows the highest sensitivity here, but for the other compounds, the values also strongly depend on the grain size of the material,

whereas powderlike materials are more sensitive and larger crystals show lower sensitivities.

Differential scanning calorimetry (DSC) measurements to determine the melt and decomposition temperatures of **1**, **3**, and **5–10** (about 1.5 mg of each energetic material) were performed in covered aluminum-containers with a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mL per minute on a Linseis PT 10 DSC^[27] calibrated by standard pure indium and zinc at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. The decomposition temperatures are given as absolute onset temperatures. The highest thermal stabilities among the investigated materials were observed for both 5-cyanotetrazolate salts **1** (263 $^{\circ}\text{C}$) and **3** (284 $^{\circ}\text{C}$). Also the tetrazole-5-carboxamide oxime (**6**) has a surprisingly high thermal stability of 244 $^{\circ}\text{C}$. Here the dehydration of the compound, which precipitates as a monohydrate as evidenced by elemental analysis, is indicated by an endothermic step in the DSC curve at 120 $^{\circ}\text{C}$. Looking at the thermal stabilities of the ionic compounds **5–10**, again the hydroxylammonium and the triaminoguanidinium salts have the lowest thermal stability (**5**: 173 $^{\circ}\text{C}$, **7**: 171 $^{\circ}\text{C}$, **10**: 160 $^{\circ}\text{C}$), whereas the ammonium and guanidinium salts decompose not below 200 $^{\circ}\text{C}$ (**8**: 202 $^{\circ}\text{C}$, **9**: 206 $^{\circ}\text{C}$).

Calculations

Several energetic parameters such as the detonation pressure, detonation velocity, and heat of explosion of **5** as well as **7–10** were calculated by the EXPLO5.05 computer code.^[28] The program is based on the input of the energy of formation (kJ kg^{-1}), density (g cm^{-3}) and the sum formula.

The heats of formation of **5** and **7–10** were also computed theoretically by using the atomization method Equation (1) in combination with CBS-4M electronic enthalpies.^[29] The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero-point energy is computed at the same level. It then uses a large basis set self-consistent-field (SCF) calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher-order contributions. In this study we applied the modified CBS-4M method (**M** referring to the use of Minimal Population localization) which is a reparametrized version of the original CBS-4 method and also includes some additional empirical corrections.^[30] This method was shown to be suitable for energetic compounds in different recent publications.^[31] The quantum chemical calculations were carried out using the Gaussian G09 program package.^[32] Coordinates of the optimized structures can be found in the Supporting Information.

$$\Delta_f H_{(g, M, 298)}^{\circ} = H_{(Molecule, 298)}^{\circ} - \sum H_{(Atoms, 298)}^{\circ} + \sum \Delta_f H_{(Atoms, 298)}^{\circ} \quad (1)$$

For the ionic compounds the gas-phase enthalpies of forma-

Table 3. Energetic properties and detonation parameters of **5** and **7–10**.

	5	7	8	9	10	2,4,6-TNT	RDX
formula	C ₂ H ₆ N ₆ O ₂	C ₂ H ₇ N ₇ O ₂	C ₂ H ₇ N ₇ O	C ₃ H ₉ N ₉ O	C ₃ H ₁₂ N ₁₂ O	C ₇ H ₅ N ₃ O ₆	C ₃ H ₆ N ₆ O ₆
<i>M_r</i> [g mol ⁻¹]	146.11	161.12	145.12	187.16	232.21	227.13	222.12
IS [J] ^[a]	40	10	40	40	15	15 ^[21]	7.5 ^[21]
FS [N] ^[b]	288	> 360	288	360	360	353	120 ^[21]
ESD-test [J] ^[c]	0.15	0.30	0.75	1.0	1.0	0.8	0.2
<i>N</i> [%] ^[d]	57.52	60.85	67.56	67.35	72.38	18.50	37.84
<i>Ω</i> [%] ^[e]	-54.75	-54.61	-71.65	-81.20	-75.78	-73.96	-21.61
<i>T</i> _{decomp} [°C] ^[f]	173	171	202	206	160	81 (m.p.), 290 (decomp)	205 (m.p.), 210 (decomp)
density [g cm ⁻³] ^[g]	1.660	1.670	1.581	1.504	1.617	1.713 (100 K) ^[41]	1.858 (90 K) ^[42]
$\Delta_f H_m^\circ$ [kJ mol ⁻¹] ^[h]	74.7	294.4	235.9	214.4	535.2	-55.5	86.3
$\Delta_f U^\circ$ [kJ kg ⁻¹] ^[i]	929.9	1950.1	1753.3	1270.8	2837.7	-168.0	489.0
EXPLO5 values							
$-\Delta_f U^\circ$ [kJ kg ⁻¹] ^[j]	4395	5168	3875	3078	4444	5258	6190
<i>T_E</i> [K] ^[k]	3036	3349	2674	2297	2827	3663	4232
<i>p_{C-J}</i> [kbar] ^[l]	258	294	230	180	271	235	380
<i>D</i> [m s ⁻¹] ^[m]	8180	8643	7962	7254	8508	7459	8983
gas vol. [L kg ⁻¹] ^[n]	819	837	827	802	841	569	734
<i>I_s</i> [s ⁻¹] ^[o]	206	230	202	182	223	205	258

[a] Impact sensitivity (BAM drophammer, method 1 of 6). [b] Friction sensitivity (BAM friction tester, method 1 of 6). [c] Electrostatic discharge device (OZM). [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC ($\beta = 5^\circ\text{C}$). [g] Estimated from X-ray analysis. [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 (isobaric conditions, chamber pressure of 60 bar).

tion (Table 2) were converted into the solid-state (standard conditions) enthalpy of formation $\Delta_f H_m$ (Table 3) by subtraction of lattice enthalpies. These lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (from XRD) according to Jenkin's equations.^[33]

Lastly, the molar standard enthalpies of formation ($\Delta_f H_m$) were used to calculate the solid state energies of formation (ΔU) per kilo according to Equation (1), where Δn is the change of moles of gaseous components.

$$\Delta_f U = (\Delta_f H_m - \Delta n \times RT) \times 1000/M \quad (2)$$

All compounds are formed endothermically in the solid state (Table 3). Triaminoguanidinium salt **10** shows the highest value of 535 kJ mol⁻¹, which is caused mainly by the three N–N bonds within the cation. The lowest heat of formation of 75 kJ mol⁻¹ is observed for **5**, which can be explained by the formal addition of one exothermically formed water molecule.

The detonation parameters and specific impulse were calculated using the latest version of the EXPLO5 code (V5.05). EXPLO5 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. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the Chapman–Jouget (CJ) point.

For all compounds their maximum X-ray densities at -173 K were used for the EXPLO5 computations. 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). The calculations were performed using the maximum densities according to the crystal structures and the results are gathered in Table 3. With respect to desired detonation performance compound **7** has the best calculated values regarding the most important values: detonation pressure ($p_{C-J} = 294\text{ kbar}$), velocity ($D = 8643\text{ m s}^{-1}$), and heat of detonation ($\Delta_f U = -5168\text{ kJ kg}^{-1}$). It has also the highest calculated specific impulse ($I_s = 230\text{ s}$). However, modern low-corrosive propellant mixtures demand low deflagration temperatures, which is ensured better by compound **10**. The detonation parameters of all investigated compounds are lower as compared to those of commonly used high explosives such as RDX (hexogen, Table 3) or HMX (octogen). However, in the case of **7** and **10**, the calculated detonation performance is significantly better than that of for example, PETN (pentaerythritol tetranitrate) and largely better than those of TNT (trinitrotoluene), which are listed in Table 3.

Conclusion

From this initial study the following conclusions can be drawn:

- Sodium 5-cyanotetrazolate sesquihydrate (**1**) was protonated with 2 M HCl to give the free acid 5-cyanotetrazole (**2**). The silver salt of **2** was prepared by treating **1** with AgNO₃.
- The hydrolysis product of **1**, tetrazole-5-carboxamide (**4**) was obtained after treating **1** with an excess of 6 M HNO₃ at 80 °C. It was deprotonated with hydroxylamine to give the hydroxylammonium salt **5**.

- Sodium 5-cyanotetrazolate sesquihydrate (**1**) can be converted into tetrazole-5-carboxamide oxime (**6**) by treatment with hydroxylammonium chloride and gave 60% yield. Treatment of 5-cyanotetrazole (**2**) with hydroxylamine yielded the same compound in 74% yield.
- Four nitrogen-rich salts of **6**, the hydroxylammonium (**7**), ammonium (**8**), guanidinium (**9**), and triaminoguanidinium tetrazole-5-carboxamide oxime (**10**) were prepared and fully characterized.
- The crystal structures of **2–5** and **7–10** were determined using low-temperature single-crystal X-ray analysis. They crystallize in the common space groups $P2_1/m^{-1}$ (**2**, **4**), $P2_1/n$ (**3**, **7**, **10**), $P2_1/c$ (**5**), $C2/c$ (**8**), and $Pca2_1$ (**9**) with densities between 1.504 g cm^{-3} (**9**), and 1.730 g cm^{-3} (**4**) for the CHNO compounds and 3.245 g cm^{-3} for the silver salt **3**.
- The sensitivities towards impact, friction, and electrostatic discharge were determined of **1**, **3**, and **5–10**. They reach from very sensitive (IS: $< 1\text{ J}$, FS: $< 5\text{ N}$, ESD: 1 mJ) for the silver salt **3** to insensitive for the guanidinium salt **9** (IS: 40 J , FS: 360 N , ESD: 1.0 J).
- The thermal stabilities of **1**, **3**, and **5–10** were determined by DSC measurements. Here, the sodium (263°C) and the silver salt (284°C) of **2** reached the highest thermal stabilities, whereas the triaminoguanidinium salt of **6** (160°C) and the hydroxylammonium salts of **4** (173°C) and **6** (171°C) decompose below 180°C .
- With the calculated heats of formation (CBS-4M) and the X-ray densities, several detonation parameters of **2**, **4**, **5**, and **7–10** were calculated (EXPLO5.05). Their detonation velocities reach from 7254 (**9**) to 8643 ms^{-1} (**7**), while having detonation pressures that reach from 180 (**9**) to 294 kbar (**7**). Therefore, the detonation parameters of all investigated compounds are lower compared to those of military high explosives such as RDX or HMX. However, in the case of **7** and **10**, the detonation performance is slightly better than that of PETN (pentaerythritol tetranitrate) and largely better than those of TNT.

Experimental Section

Experimental details

CAUTION! 5-Cyanotetrazole, tetrazole-5-carboxamide and tetrazole-5-carboxamide oxime and the salts thereof are energetic materials with increased sensitivities towards shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds.

All chemicals and solvents were used as received (Sigma–Aldrich, Fluka, Acros). ^1H and ^{13}C spectra were recorded using a JEOL Eclipse 270, JEOL EX 400, or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^1H , ^{13}C). To determine the melting and decomposition temperatures of the described compounds a Linseis PT 10 DSC (heating rate 5°C min^{-1}) was used. Infrared spectra were measured using a PerkinElmer Spectrum One FT-IR spectrom-

eter as KBr pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 equipped with a Nd-YAG-Laser (1064 nm) and a LN-Ge diode as detector. Mass spectra of the described compounds were measured at a JEOL MStation JMS 700 using either FAB, DEI, or DCI technique. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer was employed.

The crystal structures of compounds **2–5** as well as **7–10** were determined by low-temperature X-ray analysis on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection and reduction was carried out using the CrysAlisPro software.^[34] The structures were solved either with Shelxs-97^[35] or Sir-92,^[36] refined with Shelxl-97^[37] and finally checked using the Platon^[38] software integrated in the WinGX^[39] software suite. The absorptions were corrected with a Scale3 Abspack multiscan method. Selected data and parameter of the X-ray determinations are given in Table 1. Further crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre.^[40]

The detonation parameters were calculated using the program EXPLO5V5.05. The program is based on the steady-state model of equilibrium detonation and uses Becker–Kistiakowsky–Wilson equation of state (BKW E.O.S) for gaseous detonation products and Cowan–Fickett E.O.S. for solid carbon. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point.

Triaminoguanidine (free base) was synthesized by dissolving triaminoguanidinium chloride in aqueous sodium hydroxide under N_2 and addition of DMF to the mixture. Subsequently precipitated triaminoguanidine was filtered off with a Schlenk frit. Triaminoguanidinium chloride was isolated after treating aminoguanidinium bicarbonate with HCl and following reaction of the chloride with 2 equivalents of hydrazine hydrate in 1,4-dioxane under reflux conditions.

Synthesis

Sodium 5-cyanotetrazolate sesquihydrate (1**):** To a solution of sodium cyanide (50.0 g, 1.02 mol, 2.00 equiv) and sodium azide (32.5 g, 500 mmol, 1.00 equiv) in H_2O (400 mL) was added MnO_2 (50.0 g, 575 mmol, 1.15 equiv). To the resulting dark brown suspension was added dropwise a mixture of H_2SO_4 (100 mL of a 50% solution in H_2O , 936 mmol, 1.87 equiv), formic acid (60.0 g, 1.11 mol, 2.22 equiv) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.00 g, 4.01 mmol, 8.02×10^{-3} equiv) within 30 min. During this period of time the temperature was kept between 38 and 43°C by cooling the reaction mixture with an ice bath. Afterwards the mixture was heated to 60°C for 2 h before it was cooled to RT. The resulting brown slurry was filtered off and the filtrate was adjusted to pH 10 by addition of Na_2CO_3 (106 g, 1.00 mol, 2.00 equiv). The solution was diluted with H_2O (300 mL), the thus formed manganese formate was filtered off and the filtrate was neutralized with formic acid (7.00 mL). The solvent was removed under reduced pressure and the resulting residue was extracted with boiling acetone. Removal of the solvent under reduced pressure and recrystallization from ethanol/ethyl acetate yielded slightly yellow/ocher crystals of **1** (19.5 g, 135 mmol, 27%). DSC (5°C min^{-1}): m.p = 255°C , decomp = 263°C ; ^1H NMR (270 MHz, $[\text{D}_6]\text{DMSO}$, 25°C , TMS): $\delta = 3.48\text{ ppm}$ (s, 2H; H_2O); ^{13}C NMR (68 MHz, $[\text{D}_6]\text{DMSO}$, 25°C , TMS): $\delta = 138.3$ (CN_4), 115.6 ppm (CN); ^{14}N NMR (29 MHz, $[\text{D}_6]\text{DMSO}$, 25°C , CH_3NO_2): $\delta = 17.5$ (s, 2N; N(1)-

$N(2)=N(3)$, -47.7 (s, 2N); $N(1)-C(5)=N(4)$, -119 ppm (s, 1N; C-CM); IR (KBr): $\tilde{\nu}=3520$ (s), 3414 (vs), 3298 (s), 2863 (w), 2836 (w), 2474 (w), 2460 (w), 2260 (m), 2180 (w), 2142 (w), 2102 (w), 2087 (w), 1704 (m), 1670 (w), 1619 (s), 1471 (w), 1422 (w), 1380 (m), 1369 (w), 1196 (w), 1150 (w), 1055 (w), 1047 (w), 877 (w), 753 (w), 738 (w), 728 (w), 671 (w), 660 (w), 602 (w), 549 (m), 533 (m), 499 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}=3359$ (1), 2266 (100), 1420 (59), 1200 (8), 1161 (5), 1095 (10), 1084 (6), 1060 (18), 737 (2), 608 (8), 495 (9), 226 cm^{-1} (5); MS (DCI⁺): m/z calcd for $\text{C}_2\text{H}_3\text{N}_5\text{O}^+$: 113.0 [M^+]; found: 113.1; elemental analysis calcd (%) for $\text{NaC}_2\text{H}_3\text{N}_5\text{O}_{1.5}$: C 16.67, H 2.10, N 48.61; found: C 16.13, H 2.02, N 46.71; BAM drophammer: 40 J; friction tester: 160 N; ESD: 380 mJ (at grain size 100–500 μm).

5-Cyanotetrazole (2): Sodium-5-cyanotetrazolate sesquihydrate (1; 3.27 g, 22.7 mmol, 1.00 equiv) was dissolved in 2 M HNO_3 (11.4 mL, 22.7 mmol, 1.00 equiv) at RT and the solvent was carefully removed under reduced pressure at a maximum temperature of 40 °C. The residue was dried under high vacuum and suspended in dry EtOH (30 mL). Filtration and slow evaporation of the mother liquor yielded slightly greenish crystals of compound **2** (1.20 g, 12.6 mmol, 56%). After almost complete evaporation of the mother liquor further green/brown crystals of **2** (0.960 g, 10.1 mmol, 44%) were obtained. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): $\delta=14.80$ ppm (s, 1H; NH); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS): $\delta=139.2$ (CN₄), 113.3 (CN) ppm; IR (KBr): $\tilde{\nu}=3461$ (w), 3158 (m), 2979 (w), 2881 (w), 2781 (w), 2680 (w), 2548 (w), 2278 (w), 2266 (w), 2153 (w), 1947 (w), 1788 (w), 1686 (m), 1560 (w), 1513 (w), 1466 (w), 1438 (w), 1414 (w), 1393 (w), 1372 (w), 1323 (m), 1294 (s), 1222 (w), 1209 (w), 1184 (w), 1170 (m), 1112 (m), 1044 (s), 1022 (s), 976 (w), 871 (w), 834 (s), 741 (m), 697 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}=3165$ (2), 2280 (100), 1468 (14), 1439 (14), 1413 (34), 1386 (3), 1297 (4), 1221 (7), 1173 (10), 1110 (26), 1068 (15), 1024 (10), 744 (4), 725 (3), 608 (13), 542 (4), 494 (15), 214 cm^{-1} (23); MS (DEI⁺): m/z calcd for C_2HN_5^+ : 95.0 [M^+]; found: 95.0; elemental analysis calcd (%) for C_2HN_5 : C 25.27, H 1.06, N 73.67; found: C 25.41, H 1.03, N 72.44.

Silver 5-cyanotetrazolate (3): Compound **1** (432 mg, 3.00 mmol, 1.00 equiv) was dissolved in H_2O (10 mL) at RT. Afterwards an aqueous solution of AgNO_3 (10 mL, 510 mg, 3.00 mmol, 1.00 equiv) was added. A thick, white precipitate started to form immediately, which was stirred for further 15 min under the exclusion of light. The precipitate was filtered off, washed with water to remove residual NaNO_3 and air-dried. Yield: 595 mg (2.95 mmol, 98%). DSC (5 °C min^{-1}): decomp=284 °C; elemental analysis calcd (%) for C_2AgN_5 : C 11.90, N 34.68; found: C 11.99, N 34.37; BAM drophammer: <1 J; friction tester: <5 N; ESD: 1 mJ (!; at grain size <100 μm).

Tetrazole-5-carboxamide (4): Compound **1** (3.20 g, 22.2 mmol) was dissolved in 6 M HNO_3 (10 mL) and the solution was heated to 80 °C for 15 min. The solvent was removed under reduced pressure and the residue was extracted with boiling ethanol (3×100 mL). After the solvent was removed from the combined extracts, the residue was recrystallized from boiling water. Yield: 1.74 g (15.4 mmol, 69%). ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): $\delta=8.57$ (s, 1H; CONH₂), 8.19 ppm (s, 1H; CONH₂); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS): $\delta=157.2$ (CONH₂), 152.0 ppm (CN₄); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}=3361$ (3), 3250 (10), 3192 (5), 2808 (2), 1688 (42), 1649 (6), 1604 (31), 1571 (64), 1442 (38), 1298 (20), 1229 (100), 1108 (82), 1090 (79), 1059 (35), 997 (7), 804 (13), 759 (2), 696 (30), 630 (2), 511 (6), 415 (58), 241 (46), 221 cm^{-1} (24); ele-

mental analysis calcd (%) for $\text{C}_2\text{H}_3\text{N}_5\text{O}$: C 21.24, H 2.67, N 61.93; found: C 18.29, H 2.30, N 62.25.

Hydroxylammonium 5-carboxamide tetrazolate (5): Compound **4** (0.710 g, 6.28 mmol, 1.00 equiv) was dissolved in H_2O (10 mL) and hydroxylamine (0.39 mL of a 50% w/v solution in H_2O , 0.420 g, 6.36 mmol, 1.01 equiv) was added. After cooling down the solution to 2 °C, **5** crystallized from the mother liquor in 88% yield (0.810 g, 5.54 mmol). DSC (5 °C min^{-1}): decomp=173 °C; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS) $\delta=10.06$ (s, 4H; NH₃OH), 7.91 (s, 1H; CONH₂), 7.59 (s, 1H; CONH₂); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS) $\delta=163.1$ (CONH₂), 157.4 ppm (CN₄); IR (KBr): $\tilde{\nu}=3310$ (s), 3201 (m), 2985 (s), 2859 (m), 2741 (vs), 2509 (m), 2178 (w), 2106 (w), 1702 (s), 1671 (s), 1631 (m), 1616 (m), 1587 (m), 1517 (s), 1385 (m), 1334 (m), 1240 (w), 1204 (m), 1173 (m), 1114 (m), 1069 (w), 1050 (m), 1009 (m), 795 (m), 718 (m), 681 (m), 656 (m), 536 cm^{-1} (m); Raman (1064 nm, 350 mW, 25 °C): $\tilde{\nu}=3139$ (4), 2939 (5), 2723 (5), 1637 (5), 1605 (12), 1527 (53), 1395 (2), 1337 (5), 1207 (33), 1175 (26), 1115 (19), 1098 (100), 1071 (47), 1051 (19), 1011 (25), 811 (3), 783 (3), 725 (13), 521 (3), 440 (12), 310 (3), 284 (6), 250 (12), 217 cm^{-1} (10); MS (FAB⁺): m/z calcd for NH_4O^+ : 34.0 [M^+]; found: 34.0; MS (FAB⁻): m/z calcd for $\text{C}_2\text{H}_2\text{N}_5\text{O}^-$: 112.0 [M^-]; found: 112.0; elemental analysis calcd (%) for $\text{C}_2\text{H}_6\text{N}_6\text{O}_2$: C 16.44, H 4.14, N 57.52; found: C 16.66, H 3.93, N 57.08; BAM drophammer: 40 J; friction tester: 288 N; ESD: 0.15 J (at grain size 100–500 μm).

Tetrazole-5-carboxamide oxime monohydrate (6): To a solution of 5-cyanotetrazole (**2**) (1.66 g, 17.5 mmol, 1.00 equiv) in H_2O (30 mL) was added hydroxylamine (1.07 mL of a 50% w/v solution in H_2O , 1.15 g, 17.5 mmol, 1.00 equiv) at RT. Crystallization started immediately after addition and yielded **6** (1.89 g, 12.9 mmol, 74%) as colorless precipitate.

Alternatively, a solution of **1** (11.5 g; 80.0 mmol; 1.00 equiv) in water (30 mL) was treated with an aqueous solution of hydroxylammonium chloride (20 mL, 5.91 g; 85.0 mmol, 1.04 equiv). The solution was heated at reflux for 10 min, until precipitation of **6** started. The crude product was filtered off and recrystallized from hot water. The filtrate was left to stand for a few more days to improve the yield. **6** (7.01 g; 48.0 mmol; 60%) was gained as colorless solid. DSC (5 °C min^{-1}): 120 °C (H_2O), decomp=244 °C; ¹H NMR (270 MHz, [D₆]DMSO, 25 °C, TMS): $\delta=10.51$ (br. s, 1H; NH), 7.09 ppm (s, 2H; C-NH₂); ¹³C NMR (68 MHz, [D₆]DMSO, 25 °C, TMS): $\delta=150.7$ (CN₄), 144.9 ppm (C(NH₂)NOH); IR (KBr): $\tilde{\nu}=3315$ (vs), 3128 (vs), 3002 (vs), 2849 (vs), 2745 (vs), 2649 (s), 2250 (w), 2211 (w), 2141 (w), 2117 (w), 1814 (w), 1801 (w), 1712 (vs), 1650 (s), 1559 (m), 1500 (w), 1462 (m), 1394 (s), 1386 (s), 1306 (m), 1199 (w), 1173 (w), 1159 (w), 1133 (w), 1121 (w), 1092 (w), 1062 (w), 1047 (w), 1024 (w), 977 (w), 774 (s), 736 (s), 723 (s), 668 (m), 660 (m), 638 (s), 599 (m), 525 (w), 501 cm^{-1} (m); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}=3116$ (9), 1648 (9), 1578 (58), 1452 (18), 1400 (6), 1315 (13), 1199 (41), 1161 (30), 1125 (100), 1085 (84), 1062 (59), 1038 (41), 770 (17), 631 (8), 422 (47), 353 (12), 326 (9), 192 (10), 157 cm^{-1} (28); MS (FAB⁺): m/z calcd for $\text{C}_2\text{H}_4\text{N}_6\text{O}^+$: 128.0 [M^+]; found: 128.0; elemental analysis calcd (%) for $\text{C}_2\text{H}_6\text{N}_6\text{O}_2$: C 16.44, H 4.14, N 57.52; found: C 17.10, H 3.76, N 57.83; BAM drophammer: 40 J; friction tester: 252 N; ESD: 80 mJ (at grain size 100–500 μm).

Hydroxylammonium 5-carboxamide-oxime tetrazolate (7): To a suspension of **6** (0.713 g, 4.88 mmol, 1.00 equiv) in H_2O (40 mL) was added hydroxylamine (0.5 mL of a 50% (w/v) solution in H_2O , 0.539 g, 8.16 mmol, 1.67 equiv) and the resulting mixture was stirred at RT until everything was dissolved. Rapidly beginning crystallization yielded small colorless crystal needles of compound **7** (435 mg, 2.69 mmol, 55%). Crystals suitable for X-ray diffraction

were obtained by slow evaporation of a solution of **7** in DMF/H₂O (1:4). DSC (5 °C min⁻¹): decomp=171 °C; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ=12.31 (br. s, 3H; H₃N-OH), 8.47 ppm (s, 2H; C-NH₂); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS): δ=156.5 (CN₄), 148.2 ppm (CNH₂NOH); ¹⁴N NMR (29 MHz, [D₆]DMSO, 25 °C, CH₃NO₂): δ=-68.8 ppm (s, 1N; C=N-OH); IR (KBr): ν̄=3454 (s), 3366 (s), 3197 (m), 3118 (m), 3005 (m), 2906 (m), 2744 (m), 1682 (m), 1643 (m), 1542 (m), 1469 (m), 1385 (s), 1309 (m), 1273 (m), 1207 (w), 1152 (m), 1116 (m), 1045 (w), 1001 (w), 970 (m), 856 (w), 808 (m), 765 (w), 732 (w), 696 (w), 502 cm⁻¹ (w); Raman (1064 nm, 300 mW, 25 °C): ν̄=3358 (3), 1666 (38), 1604 (3), 1551 (100), 1472 (1), 1393 (3), 1315 (2), 1264 (2), 1208 (30), 1153 (18), 1118 (8), 1085 (36), 1062 (3), 1047 (3), 1002 (19), 967 (13), 818 (4), 766 (8), 654 (1), 518 (2), 444 (12), 422 (2), 362 (13), 285 (1), 217 (4), 187 (3), 146 (2), 131 (29), 120 (9), 106 (28), 95 (14), 78 cm⁻¹ (81); MS (FAB⁺): *m/z* calcd for NH₄O⁺: 34.0 [*M*⁺]; found: 34.0; MS (FAB⁻): *m/z* calcd for C₂H₃N₆O⁻: 127.0 [*M*⁻]; found: 127.0; elemental analysis calcd (%) for C₂H₇N₉O₂: C 14.91, H 4.38, N 60.85; found: C 15.42, H 4.05, N 59.98; BAM drophammer: 10 J; friction tester: >360 N, ESD: 300 mJ (at grain size 100–500 μm).

Ammonium 5-carboxamide-oxime tetrazolate (8): Compound **6** (1.47 g; 10.1 mmol; 1.00 equiv) was suspended in boiling water (25 mL) and ammonia (32%; 0.5 mL; 26.7 mmol; 2.64 equiv) was added. The suspension was heated until the reaction mixture became clear and then cooled down. The solvent was removed by rotary evaporation and **8** (1.37 g; 9.44 mmol; 93%) was afforded as colorless solid. DSC (5 °C, min⁻¹): decomp=202 °C; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ=7.3 (br. s, 1H; OH), 5.6 (br. s, 2H; NH₂), 3.5 ppm (br. s, 4H; NH₄⁺); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS): δ=156.3 (CN₄), 145.1 ppm (CNH₂NOH); ¹⁴N NMR (29 MHz, [D₆]DMSO, 25 °C, CH₃NO₂): δ=-353.4 ppm (NH₄⁺); IR (KBr): ν̄=3449 (s), 3339 (vs), 3178 (vs), 3058 (vs), 2883 (s), 2165 (vw), 1907 (w), 1679 (s), 1597 (m), 1537 (w), 1447 (s), 1384 (s), 1294 (m), 1196 (w), 1144 (w), 1103 (w), 1039 (w), 962 (s), 808 (s), 690 (m), 582 (w), 495 (w) cm⁻¹; Raman (1064 nm, 300 mW, 25 °C): ν̄=3450 (2), 3328 (5), 3242 (2), 3189 (2), 3033 (7), 2869 (3), 1913 (2), 1663 (32), 1603 (3), 1542 (100), 1452 (2), 1378 (2), 1309 (4), 1200 (34), 1144 (17), 1119 (7), 1102 (12), 1061 (43), 1039 (4), 957 (36), 819 (6), 769 (11), 662 (2), 515 (3), 430 (13), 367 (7), 325 (11), 216 cm⁻¹ (19); MS (FAB⁺): *m/z* calcd for NH₄⁺: 18.0 [*M*⁺]; found: 18.0; MS (FAB⁻): *m/z* calcd for C₂H₃N₆O⁻: 127.0 [*M*⁻]; found: 127.0; elemental analysis calcd (%) for C₂H₇N₉O: C 16.55, H 4.86, N 67.56; found: C 16.97, H 4.67, N 67.03; BAM drophammer: 40 J; friction tester: 288 N; ESD: 0.75 J (at grain size 100–500 μm).

Guanidinium 5-carboxamide-oxime tetrazolate (9): Compound **6** (1.47 g, 10.1 mmol, 2.00 equiv) was suspended in H₂O (50 mL), the suspension was brought to reflux and guanidinium carbonate was added (0.900 g, 5.00 mmol, 1.00 equiv). After boiling the suspension for 5 min, it became a clear solution. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol/water to give 1.59 g (8.50 mmol, 85%) of **9** as colorless crystals. DSC (5 °C min⁻¹): m.p.=160 °C, decomp=206 °C; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ=6.61 (s, 3H; NH₂, OH), 5.72 ppm (s, 6H; C(NH₂)₃); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS): δ=158.7 (C(NH₂)₃), 156.2 (CN₄), 146.5 ppm (CNH₂NOH); IR (KBr): ν̄=3472 (s), 3428 (s), 3351 (s), 3269 (s), 3230 (s), 3174 (vs), 2785 (m), 1673 (vs), 1655 (vs), 1605 (m), 1563 (m), 1530 (w), 1412 (w), 1389 (m), 1292 (w), 1187 (w), 1139 (w), 1082 (w), 1061 (w), 1031 (w), 934 (m), 877 (w), 807 (m), 661 (w), 571 (w), 520 cm⁻¹ (w); Raman (1064 nm, 500 mW, 25 °C): ν̄=3240 (4), 3175 (5), 1659 (14), 1607 (11), 1537 (100), 1390 (3), 1189 (37), 1140 (17), 1085 (27), 1064 (26), 1032 (5), 1011 (53), 940 (27), 806 (5), 770 (6), 663 (3), 529 (7),

490 (3), 431 (11), 341 (8), 124 (79), 110 (95), 99 (112), 75 cm⁻¹ (68); MS (FAB⁺): *m/z* calcd for CH₆N₃⁺: 60.0 [*M*⁺]; found: 60.0; MS (FAB⁻): *m/z* calcd for C₂H₃N₆O⁻: 127.0 [*M*⁻]; found: 127.1; elemental analysis calcd (%) for C₃H₉N₉O: C 19.25, H 4.85, N 67.35; found: C 19.77, H 4.77, N 66.41. BAM drophammer: 40 J; friction tester: 360 N; ESD: 1.0 J (at grain size 500–1000 μm).

Triaminoguanidinium 5-carboxamide-oxime tetrazolate (10): Compound **6** (2.56 g; 20.0 mmol; 1.00 equiv) was suspended in boiling water and triaminoguanidine (2.08 g; 20.0 mmol; 1.00 equiv) was added under nitrogen atmosphere. The solution turned red and became clear. After a short time of heating, the solution became light orange and then colorless, was filtrated and left to crystallize. **10** (3.32 g; 14.3 mmol; 72%) was afforded as orange-brown crystals. DSC (5 °C, min⁻¹): decomp=160 °C; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ=9.4 (s, 1H; OH), 8.7 (s, 3H; NH-NH₂), 5.5 (s, 2H; C-NH₂), 4.5 ppm (s, 6H; NH-NH₂); ¹³C NMR (101 MHz, [D₆]DMSO, 25 °C, TMS): δ=159.6 (C(NH₂)₃), 156.5 (CN₄), 145.7 ppm (CNH₂NOH); IR (KBr): ν̄=3851 (vw), 3319 (vs), 3211 (vs), 3104 (s), 2903 (m), 1684 (s), 1613 (s) 1536 (w), 1476 (w), 1425 (w), 1381 (m), 1334 (s), 1292 (m), 1188 (vw), 1128 (s), 1031 (w), 952 (vs), 800 (w), 770 (vw), 737 (vw), 703 (vw), 638 (m), 607 (s), 489 cm⁻¹ (vw); Raman (1064 nm, 300 mW, 25 °C): ν̄=3431 (2), 3352 (4), 3297 (6), 3297 (6), 3264 (5), 3179 (2), 1658 (28), 1611 (11), 1526 (100), 1371 (7), 1299 (2), 1181 (32), 1152 (5), 1125 (16) 1080 (31), 1048 (18), 938 (28), 881 (21), 804 (4), 770 (7), 643 (5), 485 (2), 426 (26), 409 (8), 347 (11), 294 (2), 261 (10), 199 (15), 189 (15), 148 cm⁻¹ (14); MS (FAB⁺): *m/z* calcd for CH₉N₆⁺: 105.1 [*M*⁺]; found: 105.1; MS (FAB⁻): *m/z* calcd for C₂H₃N₆O⁻: 127.0 [*M*⁻]; found: 127.2; elemental analysis calcd (%) for C₃H₁₂N₁₂O: C 15.52, H 5.21, N 72.15; found: C 16.09, H 5.01, N 72.15; BAM drophammer: 15 J; friction tester: 360 N; ESD: 1.0 J (at grain size 500–1000 μm).

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