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Investigation on the Sodium and Potassium Tetrasalts of 1,1,2,2-Tetranitraminoethane

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Abstract. With respect to high-energy dense materials with high oxygen-content, the tetrasodium salt of 1,1,2,2-tetranitraminoethane as monohydrate $Na_4TNAE·H_2O$ (**4**) and the tetrapotassium salt as dihydrate $K_4TNAE·2H_2O$ (**5**) were synthesized and reported for the first time together with their crystal structures at 173 K. Whilst **4** cannot be dehydrated the crystal water content of **5** can be removed irreversibly at 160 °C to obtain K_4TNAE (**6**) as demonstrated by DTA and TGA measurements. K_4TNAE (**6**) was demonstrated using the small scale reactivity test to be a inferior explosive to RDX and CL-20. However the anionic nitramine compound was measured to be less toxic against *Vibrio fischeri* than RDX (EC_{50}: 240 $mg·L^{-1}$) with respect to its EC_{50} value above 15070 $mg·L^{-1}$. This demonstrates that the introduction of anionic nitramine moieties is a promising concept for the stabilization of energetic materials with lower toxicity.

Introduction

1,1,2,2-Tetranitraminoethane (TNAE) (**3**) has been first published in 1980 by *Lee* et al. in China.[1] In western literature the synthesis of TNAE (**3**) appears first in a military report from 1982.[2] The scientists from Lawrence Livermore National Laboratory intended to use it as a building block for the synthesis of novel cycloaliphatic explosives containing the secondary nitramine explosophore. The excellent acid-base reactivity of TNAE (**3**) has been reported by *Daozheng* in 1991.[3] A special focus was set on the tetrasodium salt Na_4TNAE, which was reported with a crystal density of 2.11 $g·cm^{-3}$ and a detonation velocity of 8995 $m·s^{-1}$ at a density of 1.89 $g·cm^{-3}$. Despite that an X-ray structure elucidation of Na_4TNAE has not been published. It was stated that the salt is hygroscopic, which supposedly could be overcome by the coating with TNT. In 2005 *Lee* et al.[4] published the tetrapotassium salt K_4TNAE (**6**) amongst the nitrogen-rich ammonium and guanidinium derivatives. In 2011 *Szala* et al.[5] reported a synthesis of TNAE (**3**) from glycoluril (**1**) without the use of nitronium nitrate N_2O_5 and reported for the tetrasodium salt Na_4TNAE a detonation velocity of 10900 $m·s^{-1}$ in combination with a detonation pressure of 42.7 GPa for the theoretical maximum density of 2.11 $g·cm^{-3}$ based on calculations with the CHEETAH code.

In 2016 *Fischer* et al.[6] reported the synthesis of 1,1,2,2-tetranitratoethane (TNE), which is a powerful solid C,H,N,O oxidizer with a high oxygen balance $\Omega(CO_2)$ of 40.9 %. The isoelectronicity of the corresponding TNAE (**3**) tetraanion with TNE and the lack of structure elucidation by X-ray diffraction was the motivation to synthesize the sodium and potassium salt of TNAE. The outstanding energetic properties of the TNAE salts that were reported in the literature should be verified. Anionic nitramines are proposed structural motifs for the stabilization of energetic materials by ionic interactions.[7] Despite that the toxicity of the nitramine moieties in RDX (1,3,5-trinitroperhydro-1,3,5-triazine) is the essential motivation for the search of replacement compounds for this important ubiquitious military explosive.[8] Bearing four anionic nitramines the TNAE (**3**) tetraanion is an excellent model compound for the aquatic toxicity of anionic nitramines.

Results and Discussion

Synthesis

The synthetic route employed is based on the work of *Szala* et al.[5] since it does not require the use of nitronium nitrate N_2O_5 for the synthesis of tetranitroglycoluril (**2**). It was optimized in several aspects, which shall be elucidated in the following. The fundamental principle of synthetic optimization in the frame of this work is the abdication of purification steps of the unstable synthetic intermediates tetranitroglycoluril (TNGU) (**2**) and TNAE (**3**). TNGU (**2**) is known to be hydrolytically unstable[9] and TNAE (**3**) can only be properly stored at –30 °C. The NMR spectra of **3** must be recorded instantaneously due to its slow decomposition in solution. Therefore TNGU (**2**) and TNAE (**3**) were directly used as crude products without purification for further synthesis and only the stable

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salts $Na_4TNAE·H_2O$ (**4**) and $K_4TNAE·2H_2O$ (**5**) were purified by vapor diffusion recrystallization.

The synthesis starts from commercially available glycoluril (**1**), which can also be easily prepared by the acid-catalyzed condensation of urea and glyoxal.[10] **1** can be nitrated four times by the use of *in situ* generated acetyl nitrate in fuming nitric acid. For the aqueous, alkaline hydrolysis and decarboxylation of TNGU (**2**) *Szala* et al.[5] suggest the use of sodium hydroxide (3 M, aq.). Under these conditions the reaction of TNGU (**2**) is strongly exothermic and led twice to the autoignition of reactant **2** during the addition. Therefore a lower base concentration (1 M, aq.) was applied facilitating the addition of TNGU (**2**). With TNAE (**3**) in hands the synthesis of the salts could be started. For $Na_4TNAE·H_2O$ (**4**) the literature procedure[5a] was applied using methanol as solvent. The synthesis of $K_4TNAE·2H_2O$ (**5**) was carried out in water. For both salts the crude product was purified by gas-phase diffusion of methanol in a highly concentrated aqueous solution of the corresponding crude product. This cleanup step results in crystals that are suitable for X-ray structure elucidation. $K_4TNAE·2H_2O$ (**5**) can be dehydrated to K_4TNAE (**6**) at 160 °C in nearly quantitative yield (Figure 1). K_4TNAE (**6**) is not hygroscopic since the subjection of a sample to ambient conditions for two weeks did not alter the results of elemental analysis.

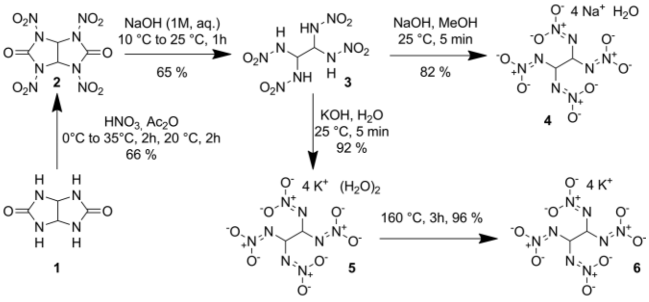

Figure 1. Synthetic route for the synthesis of the target compounds $Na_4TNAE·H_2O$ (**4**), $K_4TNAE·2H_2O$ (**5**), and K_4TNAE (**6**).

Vibrational and NMR Spectroscopy

The crystal water absorptions in the IR spectra of **4** (3476, 3246 cm^{-1}) and **5** (3486 cm^{-1}) are absent in the case of anhydrous K_4TNAE (**6**). The N–H functionality in TNAE (**3**) causes a strong IR absorption at 3236 and 3146 cm^{-1}, which is absent in the IR spectra of compounds **4**–**6**. All compounds show the characteristic absorptions of the TNAE (**3**) tetraanion. Furthermore strong absorption bands associated with the nitramine functionality can be observed at 1433/1388/1332 cm^{-1} (**4**/**5**/**6**), 1392/1332/1372 cm^{-1} and 1289/1270/1298 cm^{-1}. The NMR spectra in D_2O of **4** and **5** are almost identical with a singlet at 5.97 (**4**) and 5.95 ppm (**5**) corresponding to the C–H functionality in the proton NMR spectrum, a ^{13}C signal at $\delta = 74.6$ ppm, and a ^{14}N signal at –25 ppm corresponding to the nitro group.

X-ray Diffraction

The solid-state structures of $Na_4TNAE·H_2O$ (**4**) and $K_4TNAE·2H_2O$ (**5**) were determined by low temperature (173 K) single-crystal X-ray diffraction. Details on the measurements and refinements are given in the Supplementary Information. Cif files were deposited with the CCDC database.[11] Single crystals containing crystal water of both compounds were grown by slow diffusion of methanol into a saturated aqueous solution of the corresponding compound. The sodium salt crystallizes as a monohydrate (**4**) in the monoclinic space group $P2_1/n$, the potassium salt as a dihydrate (**5**) in the alternative space group $P2_1/c$. The densities at 173 K follow the expected trend increasing within the group of alkali metal salts (**4**: 2.060 $g·cm^{-3}$, **5**: 2.195 $g·cm^{-3}$). The molecular moieties are shown in Figure 2 and Figure 3. Both tetranitraminoethane tetraanions show very similar structures. The molecular structures are also comparable to that of 1,1,2,2-tetranitratoethane.[5] The bond lengths and angles (given in the figure captions) agree nearly perfectly with literature values. The hydrogen atoms in both structures are arranged *trans* to each other with a planar H–C–C–H torsion angle in the case of **5** (180°) and almost planar in the case of **4** (177.8°). The middle C–C bond in the tetraanions is a typical single bond (1.54 Å). Both sp^3 carbon atoms show expected tetrahedral surroundings with C–N single bonds (1.46–1.47 Å). The adjacent N–N bonds (1.27–1.28 Å) are closer to N=N double bonds (1.20 Å) which supports the nitramine Lewis structure with both negative charges on the outer oxygen atoms as depicted in Figure 1.

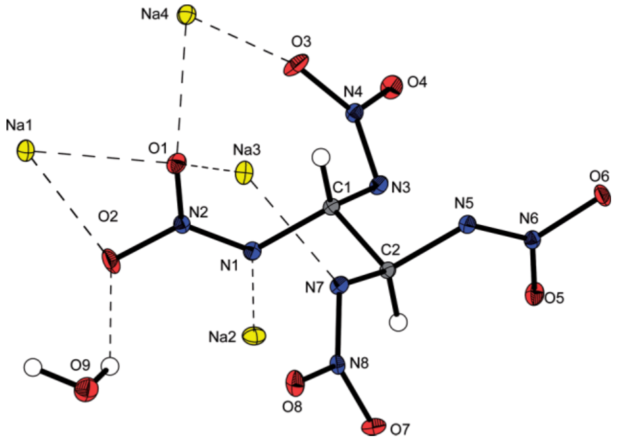

Figure 2. Molecular moiety of **4** in the crystalline state. Ellipsoids in both crystal structures drawn with Diamond2 represent the 50 % probability level. Selected bond lengths /Å: C1–C2 1.5366(15), N1–C1 1.4649(15), C1–N3 1.4599(15), N1–N2 1.2721(14), N4–N3 1.2786(14), O1–N2 1.2869(13), O2–N2 1.2842(13), N4–O3 1.2688(13), N4–O4 1.2862(13). Selected bond angles /°: N3–C1–N1 107.04(9), N4–N3–C1 112.13(9). Selected torsion angles /°: N1–C1–C2–N5 178.78(8).

Both structures form 3D networks, which are strongly dominated by the following interactions: (i) electrostatic ion interactions, (ii) classical O–H···X hydrogen bonds, (iii) non-classical O–H···X hydrogen bonds, and (iv) nitro–nitro interactions. In both structures the different alkaline metal salts do not form regular coordination polyhedrons, e.g. the octahedral coordina-

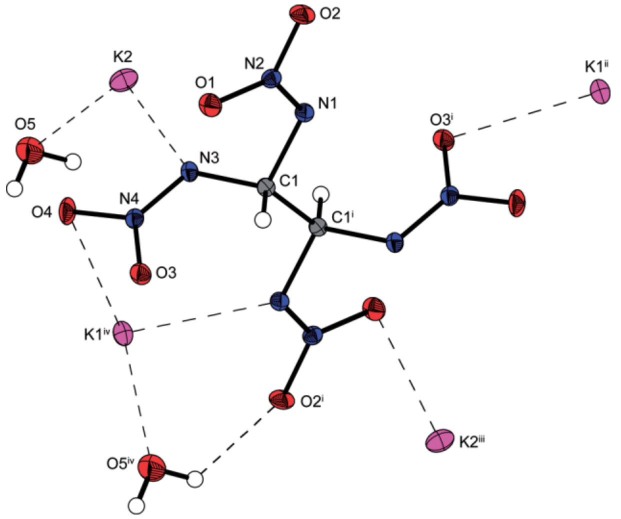

Figure 3. Molecular moiety of **5** in the crystalline state. Symmetry codes: (i) –*x*, –*y*, 1–*z*; (ii) 1–*x*, –0.5+*y*, 0.5–*z*; (iii) –*x*, –*y*, –*z*; (iv) –1+*x*, *y*, *z*. Selected bond lengths /Å: C1–C1^i 1.542(3), N1–C1 1.4628(17), N3–C1 1.4622(18), N1–N2 1.2864(16), N3–N4 1.2722(17), O1–N2 1.2709(15), O2–N2 1.2832(15), O3–N4 1.2837(16), O4–N4 1.2938(16). Selected bond angles /°: N3–C1–N1 109.78(11), N2–N1–C1 112.13(11).

tion sphere, which is oftentimes observed for sodium salts. Selected depictions on larger excerpts of the packing of $Na_4TNAE{\cdot}H_2O$ (**4**) and $K_4TNAE{\cdot}2H_2O$ (**5**) are shown in Figure 4.

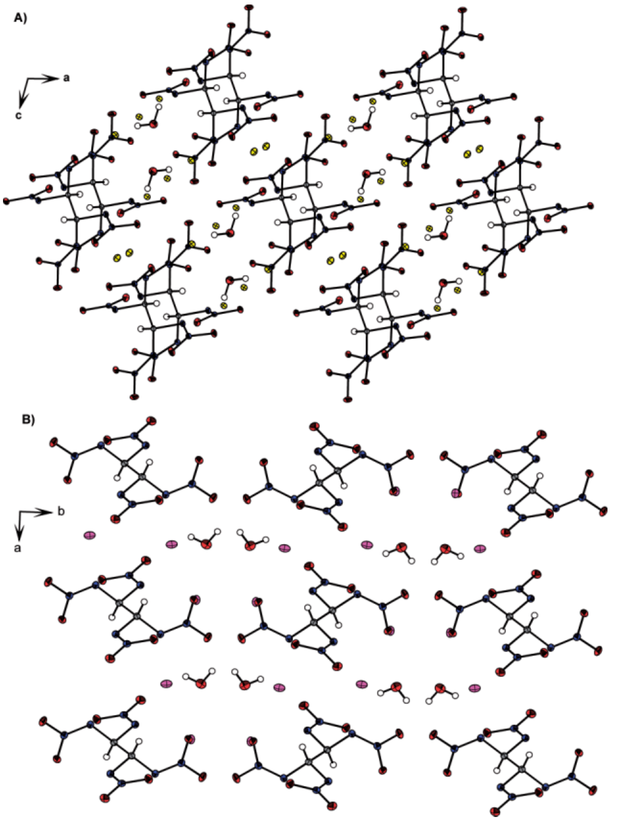

Figure 4. View on the 3D crystal structure packing: (A) along the *b* axis in $Na_4TNAE\ H_2O$ (**4**) and (B) along the *c* axis in $K_4TNAE{\cdot}2H_2O$ (**5**).

Thermogravimetric and Differential Thermal Analysis

The hydrated species $Na_4TNAE{\cdot}H_2O$ (**4**) and $K_4TNAE{\cdot}2H_2O$ (**5**) have never been described in the literature. Differential thermal analysis (DTA, see Figure 5) shows that $K_4TNAE{\cdot}2H_2O$ (**5**) loses its crystal water content at 142 °C and the unhydrated K_4TNAE (**6**) decomposes at 225 °C. (lit. value 284 °C)[4] $Na_4TNAE{\cdot}H_2O$ (**4**) decomposes without loss of water at 197 °C. (lit. value 192 °C for unhydrated species).[5a]

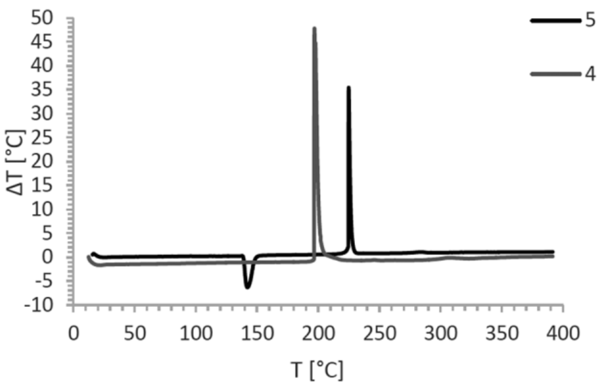

Figure 5. DTA thermogram of $Na_4TNAE{\cdot}H_2O$ (**4**) (grey line) and $K_4TNAE{\cdot}2H_2O$ (**5**) (black line). Endothermic loss of water for compound **5** at 142 °C Temperature of decomposition T_{dec}: 197 °C (**4**), 225 °C (**5**) (5 $K{\cdot}min^{-1}$ in glass vessel, T_{max} values).

$K_4TNAE{\cdot}2H_2O$ (**5**) was analyzed by thermogravimetric analysis (TGA, see Figure 6). Two water molecules (36.03 $g{\cdot}mol^{-1}$) represent 7.87 % the molecular weight of the compound (458.51 $g{\cdot}mol^{-1}$). The temperature-mass plot resulting from thermogravimetric analysis (2 $K{\cdot}min^{-1}$) shows that from 50 °C to 152 °C one molecule of water is evaporated continuously with a weight loss of 3.90 %. The second molecule of water is lost with a high mass loss rate from 152 °C to 156 °C with a total weight loss of 8.38 %, which is in agreement with the vaporization of two equivalents of water. The discrepancy of 0.51 % to the theoretical loss can be explained by sublimation of the salt in the temperature regime investi-

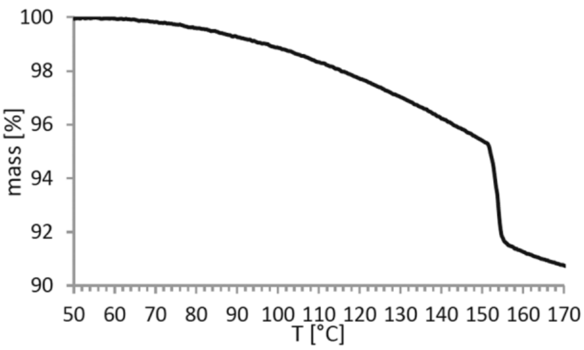

Figure 6. Thermogravimetric analysis (2 °C min^{-1}) of $K_4TNAE{\cdot}2H_2O$ (**5**). Plot of temperature /°C vs. sample weight /%. Continuous loss of mass from 50 to 152 °C, which corresponds to one equivalent of crystal water. The second crystal water equivalent is lost with a high mass loss rate in the temperature range from 152 °C to 156 °C.

gated. The sublimation of K_4TNAE (**6**) also causes the mass loss during the dehydration of **5**, which indicates a solid-gaseous phase transition without decomposition. The temperature range for water loss from TGA (142–156 °C, 2 $K\cdot min^{-1}$) is in agreement with the endothermic peak area in the DTA (138–152, 5 $K\cdot min^{-1}$).

Sensitivities

The sensitivities toward external stimuli and selected other parameters of compounds **4–6** are compiled in Table 1. Sodium salt **4** can be classified as very sensitive toward impact and sensitive toward friction. The potassium compounds **5** and **6** can be classified as sensitive toward impact and insensitive toward friction.[12] The sensitivity toward electrical discharge of all salts **4–6** is above the 50 mJ discharge that can be generated by human interaction. Compounds **4–6** possess a positive oxygen balance Ω ranging from 3.49 % to 4.25 % with the postulated combustion products CO_2, H_2O, N_2, Na_2O, and K_2O. Alternatively the same Ω values can be obtained with the metal carbonates Na_2CO_3 and K_2CO_3 as a combination of the metal oxide M_2O with CO_2. For K_4TNAE (**6**) an enthalpy of formation of –1554 $kJ\cdot mol^{-1}$ was calculated on a CBS-4M level using the Gaussian 09 software.[13] The strong exothermicity of the compound is predominantly caused by the high lattice enthalpy of the tetraanion salt and the high oxidation state of all non-oxygen atoms. The densities of all compounds are in the typical range for alkali metal salts of energetic C,H,N,O compounds.

Small Scale Reactivity Test (SSRT)

The calculation of detonation parameters relies extensively on the detonation products formed during the detonation process. In case of alkali metal salts it is hard to state, which products are formed since the presence of these metal cations might lead to the formation of metal oxides (Na_2O, Na_2O_2, K_2O), metal carbonates (Na_2CO_3, K_2CO_3) or other compounds. With this unknown detonation behavior the theoretical calculation of detonation parameters is an unreliable estimation and was not used for compounds **4–6**. Instead the Small Scale Reactivity Test (SSRT)[14] was carried out to obtain a reliable experimental benchmark parameter for the energetic performance of the water-free compound K_4TNAE (**6**). For this test a steel block with a drill hole is placed on top of an aluminum block. The drill hole is filled with the explosive and a detonator is positioned over the explosive. After the detonation a dent has been formed in the aluminum block. The dent is filled with standardized SiO_2, which is weighed. The mass ratio $\varepsilon = m(SiO_2)/m(EXP)$ is a parameter for the energetic performance of the explosive. It can be clearly stated that K_4TNAE (**6**) (ε: 0.76) is outperformed by the military explosive RDX (ε: 1.17, V_{DET}: 8983 $m\cdot s^{-1}$, p_{CJ}: 380 kbar)[8] and high-performance explosive CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) (ε: 1.72, V_{DET}: 9455 $m\cdot s^{-1}$, p_{CJ}: 467 kbar)[8]. The calculated detonation performance of Na_4TNAE (V_{DET}: 10900 $m\cdot s^{-1}$, p_{CJ}: 427 kbar) reported by *Szala* et al.,[5] which would be in the range of CL-20 should be regarded critically in comparison with the experimental performance of K_4TNAE (**6**) and CL-20 in the SSRT test. (cf. Table 2) K_4TNAE (**6**) was preferred over $Na_4TNAE\cdot H_2O$ (**4**) for the SSRT test since it does not contain crystal water.

Table 2. Results of the SSRT test.

	K_4TNAE (**6**)	RDX[8]	CL-20[8]
m(EXP)$^{a)}$	586	504	550
$m(SiO_2)^{b)}$	445	589	947
$\varepsilon = m(SiO_2)/m(EXP)$	0.76	1.17	1.72

a) Mass of explosive /mg. b) Mass of SiO_2 /mg.

Aquatic Toxicity: EC_{50}

K_4TNAE (**6**) can be considered as an aliphatic C_2H_2 unit connected to four anionic nitramines, which is highly water soluble (>662 $g\cdot L^{-1}$). Regarding the toxicity problem of RDX,[8] a cycloaliphatic triazinane containing three secondary nitramines, it is interesting to investigate the toxicity of the compound. The commercially available bioassay system LUMIStox® analyzes the toxicity of a compound towards the marine, bioluminescent bacterium *Vibrio fischeri*. For toxicological analysis the concentration which inhibits 50 % of the

Table 1. Sensitivity toward external stimuli and other selected parameters of compounds **4–6**.

	$Na_4TNAE\cdot H_2O$ (**4**)	$K_4TNAE\cdot 2H_2O$ (**5**)	K_4TNAE·(**6**)
Formula	$C_2H_4Na_4N_8O_9$	$C_2H_6K_4N_8O_{10}$	$C_2H_2K_4N_8O_8$
IS$^{a)}$ /J	2	10	4
FS$^{b)}$ /N	240	>360	>360
ESD$^{c)}$ /mJ	300	1500	1500
Grain size /µm	100–500	100–500	<100
$N^{d)}$ /%	29.80	24.44	26.52
$\Omega^{e)}$ /%	+4.25	+3.49	+3.79
$T_{dec}{}^{f)}$ /°C	197	142	225
$\rho^{g)}$ /g cm^{-3}	2.060^{i}	2.159^{i}	2.152^{j}
$\Delta_f H^{0h)}$ /$kJ\cdot mol^{-1}$	–	–	–1554

a) Impact sensitivity (BAM drophammer 1 of 6). b) Friction sensitivity (BAM friction tester 1 of 6). c) Sensitivity towards electrostatic discharge (OZM research testing device). d) Nitrogen content. e) Oxygen balance [$\Omega = w\mathrm{O} - 2\mathrm{C} - 0.5y\mathrm{H}$ – ‘$0.5M$ (M: Na or K)]. f) Decomposition temperature (T_{max} from DTA /5 K·min). g) Density. h) Calculated (CBS-4M method) enthalpy of formation. i) Density from X-ray diffraction at 173 K. j) Density from pycnometer at 298 K.

bioluminescence activity, the EC_{50} value, is determined after an incubation period of 30 min. For RDX an EC_{50} value of 240 $mg{\cdot}L^{-1}$ was observed. For K_4TNAE (**6**) a first sign of inhibition (26.7 %) could be observed at a concentration of 15070 $mg{\cdot}L^{-1}$. The final EC_{50} value will be higher than this concentration, yet it can already be stated that the toxicity of K_4TNAE (**6**) towards *Vibrio fischeri* is significantly lower by a factor >60 than RDX. This result demonstrates that anionic nitramines can be explosophores for future explosives with high biocompatibility. The introduction of anionic nitramine moieties to energetic materials has been proposed as a concept for the stabilization of novel energetic materials by ionic interactions.[7] Despite that it should be kept in mind that the bacterial strain *Vibrio fischeri* is a relatively simple organism. The environmental degradation products and toxicity towards higher life forms of this attractive model compound **6** should be further investigated.

Conclusions

The sodium salt $Na_4TNAE{\cdot}H_2O$ (**4**) and $K_4TNAE{\cdot}2\,H_2O$ (**5**) were synthesized and reported with their crystal structures at 173 K for the first time. Whereas sodium salt **4** cannot be dehydrated, the dihydrated potassium salt **5** can be dehydrated at 160 °C to K_4TNAE (**6**). This in accordance with the results of differential thermal analysis as an endotherm corresponding to a loss of water was absent in the thermogram of **4** but present in that of **5**. The loss of two equivalents of water could be demonstrated by thermogravimetric analysis of **5**. Anhydrous K_4TNAE (**6**) was outperformed by the military explosive RDX and high performance explosive CL-20 in the SSRT test. The EC_{50} value aquatic bacteria of K_4TNAE (**6**) (>15.07 $g{\cdot}L^{-1}$) is more than 60 times higher than that of RDX (0.24 $g{\cdot}L^{-1}$). Because of these results anionic nitramines were demonstrated to be a useful tool for the stabilization of energetic materials and might be suitable explosophores for high energy density materials with decreased toxicity in comparison to the widely used military explosive RDX.

Experimental Section

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics, ACBR). NMR spectra were measured with a JEOL ECX-400 and a Bruker AVANCE 400 MHz NMR instrument. The chemical shifts of the solvent peaks were adjusted according to literature values [15]. Infrared spectra were measured with a Perkin-Elmer FT-IR Spektrum BXII instrument equipped with a Smith Dura SampIIR II ATR unit. Transmittance values are described as “strong” (s), “medium” (m), and “weak” (w). Raman spectra were recorded with a Bruker RAM II device (1064 nm, 300 mW). Relative peak intensities are given in brackets. Elemental analyses (EA) were performed with a Netsch STA 429 simultaneous thermal analyzer. Sensitivity data were determined using a BAM drophammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN (OZM Research) operating with the “Winspark 1.15” software package. The particle sizes stated are valid for all sensitivity measurements. Melting and decomposition points were measured with an OZM DTA 551-EX DTA apparatus using heating rates of 5 $K{\cdot}min^{-1}$. Thermogravimetric measurements were performed with a Perkin-Elmer TGA 4000 apparatus using a heating rate of 2 $K{\cdot}min^{-1}$. Pycnometric measurements were carried out with a Quantachrome Ultrapyc 1200 e pycnometer using the large measurement cell. The EC_{50} values were determined with a Dr. Lange LUMIStox 300 luminometer.

CAUTION! All of 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 during the handling of compounds **2**–**5** at all times.

Tetranitroglycoluril (2): Glycoluril (**1**) (4.59 g, 32.30 mmol) was added whilst stirring to fuming nitric acid (81 mL, 100 %) in a 250 mL round-bottomed flask at 0 °C. The dissolution is slightly exothermic. After reaching 0 °C again, acetic anhydride (40.5 mL) was added dropwise over a period of 10 min. The temperature was lowered to 0 °C and the ice bath was removed. The reaction mixture was stirred for 2 h letting the temperature rise to 35 °C. The mixture was cooled using a water bath and was stirred for another 2 h, while keeping the temperature at 20 °C. The crude product was filtered off, washed with ice water (200 mL) and dispersed in a 3:1 mixture of chloroform and ethanol (90 mL) applying ultrasound. The colorless product was filtered off and dried in a desiccator to yield 6.83 g (65.7 %) of colorless tetranitroglycoluril **2** as crude product for further synthesis. **^{1}H NMR** (400.18 MHz, [D_6]acetone): δ = 7.77 (s, C–H). **^{13}C NMR** (100.64 MHz, [D_6]acetone): δ = 65.9 (C-H), 142.4 (C=O). **^{14}N NMR** (28.89 MHz, [D_6]acetone), δ = –57 (NO_2). **IR** (ATR): $\tilde{\nu}$ = 3735 (w), 2997 (w), 2360 (m), 2341 (m), 1825 (s), 1797 (s), 1654 (m), 1621(s), 1595(s), 1369 (w), 1298 (m), 1258 (s), 1230 (m), 1212 (m), 1182 (m), 1147 (m), 1094 (s), 957 (w), 938 (w), 848 (w), 828 (w), 810 (m), 770 (w), 742 (m), 698 (m) cm^{-1}. **RAMAN**: $\tilde{\nu}$ = 3010 (1), 2999 (22), 1827 (6), 1799 (13), 1663 (3), 1639 (7), 1598 (4), 1386 (3), 1359 (7), 1314 (48), 1271 (5), 1214 (2), 1186 (5), 1043 (4), 960 (3), 850 (7), 834 (70), 771 (3), 723 (10), 699 (6), 521 (5), 471 (3), 440 (3), 420 (10), 340 (2), 312 (45), 220 (5), 174 (4), 93 (100) cm^{-1}. **$C_4H_2N_8O_{10}$** (322.11) C 15.37 (calcd. 14.92), H 0.89 (calcd. 0.63), N 34.27 (calcd. 34.79) %. **MS** (DEI+): 322 (M^+). **IS:** >5 J, **FS:** 80 N. **ESD:** 0.2 J [<100 µm]. **DTA:** T_{begin}: 190 °C, T_{onset}: 208 °C, T_{max} 215 °C, T_{offset}: 222 °C (decomposition).

1,1,2,2-Tetranitraminoethane (TNAE) (3): A 250 mL round-bottomed flask was placed in an ice bath and sodium hydroxide (74.40 mL, 74.40 mmol, 4 equiv., aq., 1 M) solution were added. TNGU (**2**) (6.00 g, 18.63 mmol) was added in small portions whilst stirring, keeping the temperature below 10 °C. Having completed the addition, the ice bath was removed and the reaction mixture was allowed to stir for 1 h at room temperature. The reaction was quenched by the slow addition of hydrochloric acid (37.2 mL, 74.40 mmol, 4 equiv., aq., 2 M). The aqueous phase was extracted with diethyl ether (5 × 30 mL) and the combined organic phases were dried with anhydrous sodium sulfate. The drying agent was filtered off and the organic phase was removed using a rotary evaporator (0 mbar, 40 °C, 15 min). TNAE (**3**) was obtained as colorless solid with a yield of 3.25 g (65 %) as crude product for further synthesis. **^{1}H NMR** (400.18 MHz, [D_6]DMSO): δ = 6.07 (s, C–H). **^{13}C NMR** (100.64 MHz, [D_6]DMSO): δ = 63.3 (C–H). **IR** (ATR): $\tilde{\nu}$ = 3626 (w), 3480 (w), 3236 (s), 3146 (s), 3004 (m), 2361 (m), 2341 (w), 1768 (w), 1573 (s), 1448 (m), 1423 (m), 1323 (s), 1232 (s), 1162 (m), 1094 (m), 1061 (s), 930 (w), 835 (w), 774 (w), 695 (w), 667 (w) cm^{-1}. **RAMAN**: $\tilde{\nu}$ = 2997 (6), 1595 (6), 1404 (5), 1333 (18), 1162 (6), 1109 (4), 1020 (22), 934 (20), 840 (3), 828 (1), 739 (4), 677 (3), 661 (1), 601 (1), 435 (5), 344 (4), 323

(1), 296 (2), 271 (1), 245 (7), 212 (4), 96 (100) cm^{-1}. **$C_2H_6N_8O_8$** (270.12): C 9.59 (calcd. 8.89), H 2.46 (calcd. 2.24), N 40.65 (calcd. 41.48) %. **MS** (FAB-) 269 ((M–H)$^-$). **IS:** 2 J, **FS:** 30 N. **ESD:** 0.1 J [<100 µm]. **DTA:** T_{begin}: 115 °C, T_{onset}: 131 °C, T_{max} 136 °C, T_{offset}: 139 °C (decomposition).

Tetrasodium 1,1,2,2-Tetranitramidoethane Monohydrate ($Na_4TNAE{\cdot}H_2O$) (4): To methanol (250 mL) in a 500 mL round-bottomed flask was added sodium hydroxide (1.4814 g, 37.04 mmol, 4 equiv.) and mechanical stirring was applied. The obtained solution was cooled to 0 °C and TNAE (**3**) (2.5012 g, 9.26 mmol) was added in one portion. The reaction mixture was stirred for 5 min at 0 °C and methanol was removed using a rotary evaporator (30 mbar, 60 °C). The colorless residue was dried in a desiccator under high vacuum to yield 3.4012 g of crude product. For purification the crude product (2.50 g) was dissolved in distilled water (3.56 mL). The solution was filled in a 10 mL test tube, which was positioned in a vessel filled with methanol. The vessel was closed to allow vapor diffusion of methanol into the solution. After two weeks the formed crystals were collected by filtration, washed with methanol and dried in high vacuum over silica gel. 2.85 g (82 %) $Na_4TNAE{\cdot}H_2O$ **4** was obtained as colorless crystals suitable for X-ray diffraction. **^{1}H NMR** (400.13 MHz, D_2O): δ = 5.97 (s, C–H). **^{13}C NMR** (100.62 MHz, D_2O): δ = 74.6 (C–H). **^{14}N NMR** (28.91 MHz, D_2O), δ = –25 (NO_2). **IR** (ATR): $\tilde{\nu}$ = 3626 (w), 3480 (w), 3236 (s), 3146 (s), 3004 (m), 2361 (m), 2341 (w), 1768 (w), 1573 (s), 1448 (m), 1423 (m), 1323 (s), 1232 (s), 1162 (m), 1094 (m), 1061 (s), 930 (w), 835 (w), 774 (w), 695 (w), 667 (w) cm^{-1}. **RAMAN** $\tilde{\nu}$ = 2997 (6), 1595 (6), 1404 (5), 1333 (18), 1162 (6), 1109 (4), 1020 (22), 934 (20), 840 (3), 828 (1), 739 (4), 677 (3), 661 (1), 601 (1), 435 (5), 344 (4), 323 (1), 296 (2), 271 (1), 245 (7), 212 (4), 96 (100) cm^{-1}. **$C_2H_4N_8Na_4O_9$** (376.06) C 6.65 (calcd. 6.39), H 1.11 (calcd. 1.07), N 29.50 (calcd. 29.80) %. **IS:** 2 J, **FS:** 240 N. **ESD:** 0.3 J [100–500 µm]. **DTA:** T_{begin}: 190 °C, T_{onset} 195 °C, T_{max}: 197 °C (decomposition).

Tetrapotassium 1,1,2,2-Tetranitramidoethane Dihydrate ($K_4TNAE{\cdot}2H_2O$) (5): To water (120 mL) in a 250 mL round-bottomed flask was added potassium hydroxide (85 wt-%, 1.21 g, 18.19 mmol, 4 equiv.) and mechanical stirring was applied. TNAE (**3**) (1.2277 g, 4.55 mmol) was added to the obtained solution all at once. The reaction mixture was stirred for 5 min and water was removed using a rotary evaporator (30 mbar, 60 °C). The colorless crude product (1.85 g, 97 %) was dried in a desiccator. For purification the crude product (1.38 g) was dissolved in distilled water (1.92 mL). The solution was filled in a 10 mL test tube, which was positioned in a vessel filled with methanol. The vessel was closed to allow vapor diffusion of methanol into the solution. After two weeks the crystals were collected by filtration, washed with methanol and dried in high vacuum over silica gel. 1.34 g (94 %) $K_4TNAE{\cdot}2H_2O$ (**5**) was obtained as colorless crystals suitable for X-ray diffraction. **^{1}H NMR** (400.13 MHz, D_2O): δ = 5.95 (s, C–H). **^{13}C NMR** (100.62 MHz, D_2O): δ = 74.6 (C–H). **^{14}N NMR** (28.91 MHz, D_2O), δ = –25 (NO_2). **IR** (ATR): $\tilde{\nu}$ = 3746 (w), 3486 (m), 2955 (w), 2361 (m), 2337(m), 1617(w), 1388 (s), 1332 (s), 1270 (s), 1240 (s), 1124 (m), 1100 (m), 976 (m), 968 (m), 779 (m), 765 (m), 718 (w), 657 (w) cm^{-1}. **RAMAN**: $\tilde{\nu}$ = 84 (15), 110 (9), 164 (37), 194 (6), 232 (8), 281 (5), 338 (5), 390 (6), 433 (7), 538 (12), 674 (7), 713 (6), 758 (5), 1002 (16), 1018 (41), 1096 (5), 1109 (19), 1128 (5), 1292 (7), 1341 (21), 1393 (10), 1454 (27), 2028 (10), 2083 (20), 2858 (100), 2953 (25) cm^{-1}. **$C_2H_6K_4N_8O_{10}$** (458.51) C 5.46 (calcd. 5.24), H 1.26 (calcd. 1.32), N 24.47 (calcd. 24.44) %. **IS:** 10 J, **FS:** >360 N, **ESD:** 1.5 J [100–500 µm], **DTA:** T_{begin}: 137 °C, T_{onset} 139 °C, T_{max}: 142 °C (loss of water).

Tetrapotassium 1,1,2,2-Tetranitramidoethane (K_4TNAE) (6): $K_4TNAE{\cdot}2H_2O$ **5** (1.25 g, 2.73 mmol) was filled in a glass vessel, which was placed in an oven and heated from room temperature to 160 °C for 4 h. After cooling to room temperature K_4TNAE **6** (1.11 g, 96 %) was obtained as a colorless powder. **IR** (ATR): $\tilde{\nu}$ = 2956 (w), 2920 (w), 2361 (m), 2337(m), 1398 (s), 1372 (s), 1339(s), 1298 (s), 1247 (s),1129 (w), 1104 (m), 1016 (w), 1000 (w), 971(w), 958 (m), 771 (w), 743 (w), 721 (w), 657 (m) cm^{-1}. **RAMAN**: $\tilde{\nu}$ = 143 (22), 225 (3), 280 (4), 334 (3), 364 (5), 430 (4), 538 (11), 666 (4), 715 (3), 961 (6), 1004 (3), 1018 (42), 1107 (13), 1281 (3), 1340 (11), 1385 (9), 1400 (4), 1433 (13), 2028 (10), 2083 (19), 2228 (4), 2858 (100), 2925 (11), 2951 (4), 2962 (5) cm^{-1}. **$C_2H_2K_4N_8O_8$** (422.48): C 5.89 (calcd. 5.69), H 0.57 (calcd. 0.48), N 26.22 (calcd. 26.52) %. **IS:** 4 J, **FS:** >360 N. **ESD:** 1.5 J [<100 µm]. ρ_{298K} (pycnometer): 2.152 g cm^{-3}. **DTA:** T_{begin}: 208 °C, T_{onset} 224 °C, T_{max}: 225 °C (decomposition).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1408630 (**4**) and CCDC-1408628 (**5**)[11] (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Details on the X-Ray diffraction measurements and refinements of compounds **4** and **5**.

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Investigation on the Sodium and Potassium Tetrasalts of 1,1,2,2-Tetranitraminoethane