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# Energetic Metal and Nitrogen-Rich Salts of the Pentaerythritol Tetranitrate Analogue Pentaerythritol Tetranitrocarbamate

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S Supporting Information

ABSTRACT: The tetravalent pentaerythritol tetranitrocarbamate (PETNC) is deprotonated by nitrogen-rich, alkaline, alkaline earth metal, and silver bases to form the corresponding salts. Thorough analysis and characterization by multinuclear NMR, vibrational spectroscopy, elemental analysis, thermoanalytical techniques, and single crystal X-ray diffraction was performed. Furthermore, the energies of formation for the nitrogen-rich salts were calculated utilizing the Gaussian program package. The detonation performances were calculated with the Explo5 (V6.03) computer code, and the sensitivities toward impact and friction were determined and compared to the neutral PETNC and pentaerythritol tetranitrate (PETN). Ecotoxicological studies of the ammonium and guanidinium salt using Vibrio fischeri bacteria complete this study.



### INTRODUCTION

Pentaerythritol is a commercially available tetravalent alcohol with a neopentane backbone. It is a common source for energetic materials, such as pentaerythritol tetranitrate (PETN, Nitropenta),<sup>1</sup> which is used in detonators and, along with RDX, is the main ingredient in SEMTEX.<sup>2</sup> More recently, silicon-based pentaerythritol derivatives [Si(CH<sub>2</sub>N<sub>3</sub>)<sub>4</sub> and  $Si(CH_2ONO_2)_4$  were synthesized but are too sensitive for practical application.<sup>3</sup> The less sensitive sila-nitrocarbamate derivative of PETN was also very recently investigated in our group, however its performance data are not favorable.<sup>4</sup> Nitrocarbamates in general gained more attention in the field of energetic materials chemistry.<sup>5-9</sup> Due to their resonance effects, which lead to a reduction in the electrophilicity of the carbonyl group, they are relatively stable toward acid hydrolysis.<sup>10</sup> The high stability allows the nitration of carbamates using rough reaction conditions, like fuming nitric acid and concentrated sulfuric acid. Also, salt formation is possible, taking into account the increase of the acidity of the amino-hydrogen next to the electron withdrawing nitro group. Pentaerythritol tetranitrocarbamate (PETNC) combines the easy availability of pentaerythritol and the valuable properties of nitrocarbamates.<sup>11</sup> After our reports on trinitroethyl nitrocarbamate (TNENC),<sup>7,8</sup> others were very quick to prepare the first organic salts of TNENC and examine their properties, however with low thermal stability.<sup>12,13</sup> Up to now, PETNC and its ammonium salt were investigated, whereby PETNC shows better thermal stability, better sensitivity values, and density comparable to that of PETN. The ammonium salt is even less sensitive than PETNC, however its density is lower. Concerning the energetic parameters, such as the calculated

detonation velocity and experimental small-scale reactivity test, PETN is the superior compound. Though PETNC was investigated with underwater explosion tests and showed acceptable performance values.<sup>14</sup> In this work, new nitrogenrich salts, as well as selected metal salts of PETNC, are presented. These salts allow the determination of the aquatic toxicity of the PETNC anion. Furthermore, some alkali and alkaline earth metal salts may serve as potential flame colorants.

# RESULTS AND DISCUSSION

Synthesis. The previously described synthesis of primary carbamates was based on two steps, starting from a reaction of the respective alcohol with toxic phosgene to the chloroformate and subsequent treatment with ammonia.<sup>15</sup> A more convenient route is using the reactive chlorosulfonyl isocyanate (CSI) in a one-step synthesis, followed by feasible aqueous workup.<sup>16</sup> CSI was discovered in Germany in 1956; nowadays, it is a commercially available reagent giving easier access to the corresponding carbamate.<sup>17,18</sup> Using CSI, pentaerythritol tetracarbamate was synthesized in high yield and purity and subsequently nitrated to pentaerythritol tetranitrocarbamate (PETNC) with mixed acid as outlined in Scheme 1.

PETNC has four acidic nitramine hydrogen atoms which can easily be deprotonated. Analoguous to the tetraammonium salt,<sup>11</sup> nitrogen-rich, alkaline, and alkaline earth metal and silver salts were obtained by the reaction of the free bases with

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 $O_2N$ 

NO<sub>2</sub>



PETNC in aqueous solution (Scheme 2). However, attempts to prepare hydrazinium or hydroxylammonium salts failed.

The salt formation proceeds conveniently in aqueous solution at ambient temperature (except the guanidinium salt **2** had to be heated to reflux), and colorless solids are obtained in 63% up to quantitative yields. The metal salts form hydrates;

their water content was calculated from the elemental analysis values, except for the sodium salt 5 (extremely hygroscopic and viscous). In addition, the water content was confirmed in most cases using thermal gravimetric analysis (TGA, Figure 2). Due to the general low solubility of silver salts in water, silver salt 10 was synthesized with acetonitrile as solvent. Ag<sup>+</sup> is known

to form a stable diacetonitrile cationic complex [Ag- $(CH_3CN)_2$ ]<sup>+</sup>. However, it was not possible to determine the exact solvate content; therefore, this is denoted accordingly as shown in Scheme 3.<sup>19,20</sup>

NMR and Vibrational Spectroscopy. In the NMR spectra, some trends are observed. In the <sup>1</sup>H NMR spectra the resonances of the  $CH_2$  groups of the tetranitrocarbamates are found at 3.81-3.91 ppm and therefore shifted upfield compared to PETNC ( $\delta$  = 4.15 ppm) due to deprotonation.<sup>11</sup> This is consistent with the  $CH_2$ -signal of the ammonium salt which is shifted to 3.88 ppm. Comparable tendencies are observed in the <sup>13</sup>C NMR spectra. The resonance of the carbonyl carbon atom in neutral PETNC is located at 148.9 ppm and the resonances for the salts are found at lower field between 158.8-160.5 ppm. The <sup>13</sup>C NMR resonances of the neopentane skeleton remain unaffected upon deprotonation of PETNC. The resonances of the cations guanidinium and aminoguanidinium are detected at 158.0 ppm (2) and 158.9 ppm (3). In the  $^{14}$ N NMR spectra the resonances for the nitro groups of salts 2-8 can be detected as broadened signals between -2 and -13 ppm. The resonances for the nitrile solvate of 10 are found at  $\delta$  = 2.07 ppm in the <sup>1</sup>H NMR, at  $\delta$  = 118.1 ppm in the  ${}^{13}C{}^{1}H$  NMR and at -134.9 ppm in the <sup>14</sup>N NMR spectra. The resonance of the silver-acetonitrile cation was detected at 255 ppm in the <sup>109</sup>Ag NMR spectrum with DMSO- $d_6$  as solvent. A comparison with a previous <sup>109</sup>Ag NMR study of solvate-free silver nitroformate solutions in various solvents revealed, that the shift of 255 ppm is in between those of 181 ppm (DMSO) and 430 ppm (acetonitrile) of  $Ag[C(NO_2)_3]^{21}$  This deviation can be explained by solvate exchange between Ag<sup>+</sup>-acetonitrile and the DMSO solvent.

In the vibrational spectra (IR and Raman, see the Supporting Information), the characteristic strong carbonyl stretching vibrations are located in the range of  $\tilde{\nu} = 1688-1651 \text{ cm}^{-1}$ , which are in range of the NH<sub>4</sub><sup>+</sup> salt.<sup>11</sup> For the metal salts no N-H vibrations can be found in the Raman spectra in the range of  $\tilde{\nu} = 3450-3200 \text{ cm}^{-1}$ , due to deprotonation. Because of the predominant hydrate water which overlaps this particular region, no statement can be made throughout the IR spectra. The N-H stretching vibrations for hydrate-free guanidinium salt **2** and aminoguanidinium salt **3** are located at  $\tilde{\nu} = 3415-3208 \text{ cm}^{-1}$ .

**Single-Crystal Structure Analysis.** Single crystals suitable for X-ray diffraction measurements were obtained for aminoguanidinium salt 3 by recrystallization from water. The molecular structure of 3 is shown in Figure 1, which crystallizes as a colorless block in the triclinic space group  $P\overline{1}$  with two molecules per unit cell and a density of 1.65 g cm<sup>-3</sup> at 123 K.

The structure of 3 is similar to that of the ammonium salt.<sup>11</sup> The nitro groups are rotated out of plane of the nitrocarbamate moiety, as demonstrated by the torsion angle O3-N2-O1-C3 (-12.5°). For the nitramine moiety, the N1–N2 bond length is 1.344 Å, which is shorter than the neutral compound (1.379 Å) and more comparable to the N1–N2 bond length of the NH<sub>4</sub><sup>+</sup> salt (1.332 Å).<sup>11</sup> For PETNC, this indicates a substantial double-bond character, achieved by delocalization of the nitrogen lone pair of N1, which is more substantial for the salts.

**Physical and Energetic Properties.** The physical and energetic properties of the salts 2–9 were determined and are summarized in Tables 1 and 2. PETNC and 1 were recalculated using version 6.03 of Explos.<sup>22</sup> Concerning the



Figure 1. Crystal structure of tetrakis-aminoguanidinium pentaerythritol tetranitrocarbamate 3. Selected distances [Å] and angles [°]: C3–N1 1.370(2), C3–O2 1.215(2), C3–O1 1.366(2), C2–C1 1.536(2), C2–O1 1.438(2), C2–H7 0.98(2), C2–H8 0.96(2), N1– N2 1.344(2), N2–O3 1.243(2), N2–O4 1.238(2), N2–C3–O2 132.1(1), N2–C3–O1 105.0(1), O2–C3–O1 122.8(1), C1–C2– O1 113.5(1), N1–N2–O3 114.1(1), N1–N2–O4 124.9(1), O3– N2–O4 120.9(1), C3–N1–N2 117.4(1), C3–O1–C2 118.1(1).

energetic properties of the nonmetal salts 1–3, aminoguanidinium salt 3 is in the range of TNT in terms of detonation velocity ( $V_{det} = 6950 \text{ m s}^{-1}$ ).<sup>2</sup> Nevertheless, PETN and PETNC are still superior in terms of these properties.

With decomposition temperatures of 136 °C (1), 180 °C (2), 149 °C (3), 186 °C (4), 156 °C (5), 177 °C (6) 161 °C (7), 152 °C (8), and 176 °C (9), the salts 2, 4, 6, 7, and 9 show an appropriate thermal stability. The thermally most stable salt was the lithium salt 4 with a decomposition temperature of 186 °C. The neutral PETNC is still the thermally most stable compound. The sensitivities toward impact and friction were determined with a BAM Drophammer<sup>24</sup> and a BAM Friction Tester.<sup>25</sup> The salts were then classified according the UN recommendations on the transport of dangerous goods;<sup>26</sup> therefore, we considered 1–3 as insensitive and 7–9 as less sensitive. Only the lithium (4) and potassium (6) salts show impact sensitivities in the range of sensitive compounds (20 and 7 J).

When comparing the room-temperature densities of the synthesized salts, 1 ( $\rho = 1.62 \text{ g cm}^{-3}$ ) and 3 ( $\rho = 1.64 \text{ g cm}^{-3}$ ) show acceptable values; however, only the density of PETNC ( $\rho = 1.76 \text{ g cm}^{-3}$ ) is in the range of PETN ( $\rho = 1.78 \text{ g cm}^{-3}$ ).<sup>11</sup>

TGA measurements of salts 4-9 at a heating rate of 5 °C min<sup>-1</sup> revealed a starting weight loss in a temperature range of 103–108 °C, which was not observed in the TGA measurement of PETNC (Figure 2). This leaving hydrate water is consistent with the hydrate water calculated from elemental analysis.

Additionally, the flame colors of the alkaline and alkaline earth salts were tested with a small-scale setup in a Bunsen burner flame, as these metals are known to show visible flame colors and could be useful in terms of pyrotechnical applications. Thereby, PETNC salts 4-8 combusted with a visible flame color as expected (see the Supporting Information), except for low solubility barium salt 9. Further efforts are conducted to establish the potential use in pyrotechnical formulations.

## Table 1. Physical and Energetic Properties of Salts 1–3 Compared to PETNC and PETN

	<b>1</b> <sup>11</sup>	2	3	PETNC	PETN				
formula	$C_9H_{24}N_{12}O_{16}$	$C_{13}H_{32}N_{20}O_{16}$	$C_{13}H_{36}N_{24}O_{16}$	$C_9H_{12}N_8O_{16}$	$C_5H_8N_4O_{12}$				
$M [g mol^{-1}]$	556.36	724.52	784.58	488.24	316.14				
$T_{\text{dec}} [^{\circ}C]^{a}$	136	180	149	196	165				
IS $[J]^{b}$	>40	>40	>40	8	3				
FS $[N]^c$	>360	>360	>360	360	60				
$\text{ESD} [J]^d$	>1.0	>1.5	>1.5	0.75	0.50				
$\rho [g \text{ cm}^{-3}]^e$	1.64	1.49 (pyc.)	1.62	1.76	1.78				
$N \ [\%]^f$	30.2	38.7	42.9	23.0	17.7				
O [%] <sup>g</sup>	46.1	34.6	54.5	3.3	60.7				
$\Omega_{\rm CO} \left[\%\right]^h$	-14.4	-28.7	-30.6	3.3	15.2				
$\Omega_{\mathrm{CO}_2} \left[\% ight]^i$	-40.3	-57.4	-57.1	-26.2	-10.1				
$\Delta H_{\rm f}^{\circ}  [\rm kJ  mol^{-1}]^{j}$	-2378	-2306	-1882	-1311	-561				
Explo5 v6.03									
$-\Delta_{\mathrm{Ex}}U^{\circ} \ [\mathrm{kJ} \ \mathrm{kg}^{-1}]^{k}$	1996	1735	2219	3826	5980				
P <sub>CI</sub> [kbar] <sup>k</sup>	174	134	181	242	319				
$V_{\text{det}} \left[ \text{m s}^{-1} \right]^{k}$	7028	6336	7307	7686	8405				
$V_{\rm o} \left[ {\rm L \ kg^{-1}} \right]^k$	856	866	890	718	743				

<sup>*a*</sup>Onset decomposition point  $T_{dec}$  from DSC measurement carried out at a heating rate of 5 °C min<sup>-1</sup>. <sup>*b*</sup>Impact sensitivity. <sup>*c*</sup>Friction sensitivity. <sup>*d*</sup>Sensitivity toward electrostatic discharge. <sup>*e*</sup>RT densities are recalculated from X-ray densities or measured by gas pycnometer (pyc.). <sup>*f*</sup>Nitrogen content. <sup>*b*</sup>Oxygen content. <sup>*h*</sup>Oxygen balance assuming the formation of CO and <sup>*i*</sup>CO<sub>2</sub>. <sup>*j*</sup>Enthalpy and of formation calculated by the CBS-4 M method using Gaussian 09.<sup>23</sup> <sup>*k*</sup>Predicted heat of combustion, detonation pressure, detonation velocity, and volume of gaseous products calculated by using the Explo5 (version 6.03) program package.<sup>22</sup>

#### Table 2. Physical Properties of Metal Salts 4-9

	4	5	6	7	8	9
formula	$Li_4C_9H_8N_8O_{16}$ ·2.5 H <sub>2</sub> O	$Na_4C_9H_8N_8O_{16}{\cdot}xH_2O$	$K_4 C_9 H_8 N_8 O_{16} \cdot 2 H_2 O$	$Ca_2C_9H_8N_8O_{16}\cdot 7H_2O$	$Sr_2C_9H_8N_8O_{16}.7H_2O$	$Ba_2C_9H_8N_8O_{16}{\cdot}4H_2O$
$M [g \text{ mol}^{-1}]$	557.00	d	676.63	690.46	785.55	830.92
$T_{\text{dec}} [^{\circ}C]^{a}$	186	156	177	161	152	176
IS $[J]^{b}$	20	d	7	40	40	35
FS $[N]^c$	360	d	360	360	360	360

<sup>a</sup>Onset decomposition point  $T_{dec}$  from DSC measurement carried out at a heating rate of 5 °C min<sup>-1</sup>. <sup>b</sup>Impact sensitivity. <sup>c</sup>Friction sensitivity. <sup>d</sup>The values of the sodium salt 5 were not determined, because of its high hygroscopicity.



Figure 2. TGA measurements of PETNC (left) and the tetralithium salt 4 (right) at a heating rate of 5 °C min<sup>-1</sup>.

**Toxicity Assessment.** In order to determine the ecotoxicological impact of water-insoluble PETNC, the  $EC_{50}$  (effective concentration) values of ammonium salt 1 and guanidinium salt 2 were measured.  $EC_{50}$  refers to the concentration of a toxicant which induces a response of 50% after a specific exposure time. The method used herein was based on bioluminescent *Vibrio fischeri* NRRL-B-11177 marine

bacteria strains whose luminescent is inhibited when exposed to a toxicant. Therefore, the  $EC_{50}$  is defined as the concentration level where the bioluminescence is halfway decreased. All measurements started with the determination of the bioluminescence of untreated reactivated bacteria. After exposure times of 15 and 30 min, the bioluminescence was determined. The resulting effective concentration leads to a classification of the compounds as nontoxic (>1.00 g L<sup>-1</sup>), toxic (0.10–1.00 g L<sup>-1</sup>), and very toxic (<0.10 g L<sup>-1</sup>).<sup>27</sup> Our own previous results on RDX<sup>28</sup> proved that the half-maximum effective concentration of RDX [EC<sub>50</sub> (30 min) = 0.24 g L<sup>-1</sup>] is in the range of toxic compounds [lit.: EC<sub>50</sub> (30 min) = 0.27 g L<sup>-1</sup>].<sup>29</sup> Ammonium salt 1 did not lead to an inhibition of the bioluminescence up to 10% after 15 and 30 min using a solution with c = 2.02 g L<sup>-1</sup>. Guanidinium salt 2 was measured in higher concentrations and revealed an EC<sub>50</sub> value of 2.86 g L<sup>-1</sup> at 15 min and of 1.42 g L<sup>-1</sup> at 30 min. Therefore, the PETNC anion can be considered nontoxic according to *Vibrio fischeri*.

# CONCLUSIONS

New nitrogen-rich, alkaline, alkaline earth metal, and silver salts of PETNC were synthesized and thoroughly characterized by various analytical methods. The thermal stability of guanidinium salt 2 is in a promising range (180 °C), and the detonation velocity of aminoguanidinium salt 3 is almost in the range of PETNC. All salts are of remarkably low sensitivity against impact, friction and electrostatic discharge. The burning behavior of metal salts 4-8 show a combustion with a visible flame color, as to be expected for alkali and alkaline earth metal salts. Nevertheless, more efforts are necessary to find a practical application for salts 4-8 in pyrotechnic formulations based on their visible flame color. The tested ammonium and guanidinium salt are considered nontoxic according to Vibrio fischeri. Further tests should show if PETNC could have a potential application as nontoxic and stable safe-handling PETN alternative.

# EXPERIMENTAL SECTION

**General.** Solvents, deuterated solvents of NMR experiments, and all further chemicals were used as received from the suppliers, without further purification. NMR spectra were recorded with a Bruker 400 or Bruker 400 TR at ambient temperature. The chemical shifts were determined with respect to external standards, Me<sub>4</sub>Si (<sup>1</sup>H 399.8 MHz; <sup>13</sup>C 100.5 MHz), MeNO<sub>2</sub> (<sup>14</sup>N 28.9 MHz), and AgNO<sub>3</sub> (<sup>109</sup>Ag 18.6 MHz).

Infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR ATR device. Raman spectra were recorded in a glass tube with a Bruker MultiRAM FT-Raman spectrometer with ND:YAG laser with excitation up to 1000 mW at 1064 nm in the range 4000–400  $\text{cm}^{-1}$ . All spectra were recorded at ambient temperature.

Analyses of C/H/N contents were performed with an Elementar vario EL or Elementar vario micro cube. Melting and decomposition points were measured with a Linseis DSC-PT10 apparatus with a heating rate of 5 °C min<sup>-1</sup> in a temperature range 25–400 °C and partly by thermal gravimetric analysis (TGA) with a PerkinElmer TGA4000.

The sensitivities toward impact and friction were determined with a BAM drophammer<sup>24</sup> and a BAM friction tester.<sup>25</sup> The sensitivity toward electrostatic discharge was determined with an electric spark tester from OZM.

The toxicity assessments were carried out as described by the provider using a LUMI-Stox 300 spectrometer, obtained by HACH LANGE GmbH. According to DIN/EN/ISO 11348, a 10-point dilution series was prepared (without G1 level) with a known weight of the salts and a 2% NaCl stock solution.<sup>29</sup>

Single crystal X-ray diffraction studies were performed on an Oxford Diffraction XCalibur3 diffractometer with a generator (voltage 50 kV, current 40 mA) and a KappaCCD area detector operating with Mo K $\alpha$  radiation ( $\lambda = 0.7107$  Å). The solution of the structure was performed by direct methods using SIR97<sup>30,31</sup> and refined by full-matrix least-squares on  $F^2$  (ShelXL)<sup>32,33</sup> implemented in the WinGX

software package<sup>34</sup> and finally checked with the Platon software.<sup>35</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located on a difference Fourier map. Diamond plots are shown with thermal ellipsoids at the 50% probability level.

The theoretical calculations were carried out by using the program package Gaussian 09<sup>23</sup> and were visualized by GaussView 5.08.<sup>3</sup> Structural optimizations and frequency analyzed were performed at the B3LYP level of theory (Becke's BE three parameter hybrid functional using the LYP correlation functional). For C, H, N, and O, a correlation-consistent polarized double- $\zeta$  basis set cc-pVDZ was used. The enthalpies (H) and free energies (G) were calculated on the CBS-4 M level of theory (complete basis set). CBS-4 M starts with a HF/3-21G(d) geometry optimization, an initial guess for the following SCF calculation as base energy. This finishes with a final MP2/6-31+G calculation with a CBS extrapolation to correct the energy in second order. For an approximation of higher order contributions, implementations of MP4(SDQ)/6-31+(d,p) and additional empirical corrections are required. The enthalpies of the gas-phase species were estimated according to the atomization energy method.<sup>37</sup> The gas-phase enthalpies of formation were converted into the solid-state values using the lattice energy equation provided by Jenkins. $^{38-41}$  All calculations affecting the detonation parameters were based on condensed phase enthalpies of formation and carried out by using the program package Explo5 V6.03.<sup>22</sup>

**Caution!** Pentaerythritol tetranitrocarbamate (PETNC) and potentially the metal salts are considered as sensitive materials and therefore should be handled with caution during synthesis or manipulation, and additional protective equipment (leather jacket, face shield, ear protection, Kevlar gloves) is strongly recommended.

General Procedure for the Salt Preparation (2–9). Various amounts of PETNC (0.5-1 mmol) in 5–10 mL water are stirred and to this suspension equimolar amounts of the base (guanidinium carbonate; aminoguanidinium bicarbonate; hydroxides of lithium, sodium, potassium, calcium, strontium, and barium) was added at ambient temperature. The resulting mixture is further stirred for 1–2 h (additionally 1 h at 100 °C for guanidinium carbonate) or 12 h (Ca, Sr, Ba). In the case of Ca/Sr/Ba the precipitate is filtered and dried. In all other cases, the water is removed *in vacuo* and the PETNC salts isolated (2 83%, 3 100%, 4 65%, 5 100%, 6 93%, 7 82%, 8 63%, 9 79%).

Tetrakis(guanidinium) PETNC (2). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.08 (s, 24H, NH<sub>2</sub>), 3.84 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 159.4 (CO), 158.0 (C(NH<sub>2</sub>)<sub>2</sub>), 63.5 (CH<sub>2</sub>), 41.3 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -7 (NO<sub>2</sub>) ppm. EA: C<sub>13</sub>H<sub>32</sub>N<sub>20</sub>O<sub>16</sub> (724.52): calcd C 21.55, H 4.45, N 38.66%. Found C 21.56, H 4.35, N 38.57%. IS: 40 J (grain size <100 µm). FS: 360 N (grain size < 100 µm). ESD: 1.50 J (grain size < 100 µm). DSC (5 °C min<sup>-1</sup>): 180 °C (dec.).

Tetrakis(aminoguanidinium) PETNC (**3**). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 8.60 (br, 4H, NHNH<sub>2</sub>), 7.14 (br, 16H, C(NH<sub>2</sub>)<sub>2</sub>), 4.68 (s, 8H, NHNH<sub>2</sub>), 3.84 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ = 159.7 (CO), 158.9 (C(NH<sub>2</sub>)), 63.1 (CH<sub>2</sub>), 41.7 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO): δ = -2 (NO<sub>2</sub>) ppm. EA: C<sub>13</sub>H<sub>36</sub>N<sub>24</sub>O<sub>16</sub> (784.58): calc. C 19.90, H 4.62, N 42.85%. Found C 20.03, H 4.51, N 42.61%. IS: 40 J (grain size < 100 µm). FS: 360 N (grain size < 100 µm). ESD: 1.50 J (grain size < 100 µm). DSC (5 °C min<sup>-1</sup>): 149 °C (dec.).

Tetralithium PETNC-2.5 hydrate (**4**). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.81 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 159.8 (CO), 62.0 (CH<sub>2</sub>), 42.0 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -7 (NO<sub>2</sub>) ppm. EA: Li<sub>4</sub>C<sub>9</sub>H<sub>8</sub>N<sub>8</sub>O<sub>16</sub>·2.5 H<sub>2</sub>O (557.00): calc. C 19.41, H 2.35, N 20.12%. Found C 19.56, H 2.39, N 19.98%. IS: >20 J (grain size < 100  $\mu$ m). FS: 360 N (grain size < 100  $\mu$ m). ESD: 1.50 J (grain size < 100  $\mu$ m). DSC (5 °C min<sup>-1</sup>): 186 °C (dec.).

Tetrasodium PETNC·x hydrate (5). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.88 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 159.8 (CO), 62.2 (CH<sub>2</sub>), 42.1 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -13 (NO<sub>2</sub>) ppm. DSC (5 °C min<sup>-1</sup>): 156 °C (dec.).

Tetrapotassium PETNC-2 hydrate (**6**). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.88 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 158.8 (CO), 62.3 (CH<sub>2</sub>), 42.1 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -12 (NO<sub>2</sub>)

ppm. EA:  $K_4C_9H_8N_8O_{16}$ : 2  $H_2O$  (676.63): calc. C 15.98, H 1.79, N 16.56%. Found C 16.51, H 2.15, N 16.77%. IS: 7 J (grain size 100–250  $\mu$ m). FS: 360 N (grain size 100–250  $\mu$ m). DSC (5 °C min<sup>-1</sup>): 177 °C (dec.).

Dicalcium PETNC-7 hydrate (7). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.86 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 160.4 (CO), 62.3 (CH<sub>2</sub>), 42.1 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -8 (NO<sub>2</sub>) ppm. EA: Ca<sub>2</sub>C<sub>9</sub>H<sub>8</sub>N<sub>8</sub>O<sub>16</sub>.7 H<sub>2</sub>O (690.46): calc. C 15.66, H 3.21, N 16.23%. Found C 15.88, H 3.24, N 16.16%. IS: 40 J (grain size < 100 μm). FS: 360 N (grain size < 100 μm). ESD: 1.50 J (grain size < 100 μm). DSC (5 °C min<sup>-1</sup>): 167 °C (dec.).

Distrontium PETNC-7 hydrate (8). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.91 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 160.5 (CO), 62.5 (CH<sub>2</sub>), 42.1 (C) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -7 (NO<sub>2</sub>) ppm. EA: Sr<sub>2</sub>C<sub>9</sub>H<sub>8</sub>N<sub>8</sub>O<sub>16</sub>·7 H<sub>2</sub>O (785.55): calc. C 13.76, H 2.82, N 14.26%. Found C 13.29, H 2.41, N 12.43%. IS: 40 J (grain size < 100 µm). FS: 360 N (grain size < 100 µm). ESD: 1.50 J (grain size < 100 µm). DSC (5 °C min<sup>-1</sup>): 152 °C (dec.).

Dibarium PETNC-4 hydrate (9). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.91 (s, 8H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 160.3 (CO), 62.5 (CH<sub>2</sub>), 42.0 (C) ppm. <sup>14</sup>N NMR (not visible due to low solubility). EA: Ba<sub>2</sub>C<sub>9</sub>H<sub>8</sub>N<sub>8</sub>O<sub>16</sub>·4 H<sub>2</sub>O (830.92): calc. C 13.01, H 1.94, N 13.49%. Found C 13.03, H 1.82, N 13.38%. IS: 35 J (grain size < 100 μm). FS: 360 N (grain size < 100 μm). ESD: 0.80 J (grain size < 100 μm). DSC (5 °C min<sup>-1</sup>): 156 °C (dec.).

Silver PETNC (10). Pentaerythritol tetranitrocarbamate (143 mg, 0.3 mmol) was suspended in dry acetonitrile (10 mL) and silver carbonate (163 mg, 0.6 mmol) was added at 0 °C under exclusion of light. Immediately within 10 min, the PETNC dissolved, impurities were filtered, and the solution was evaporated in the dark at ambient temperature. Silver pentaerythritol tetranitrocarbamate (10) was obtained as a colorless solid in 86% yield. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 4.03 (s, 8H, CH<sub>2</sub>), 2.07 (s, 6H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 157.2 (CO), 118.1 (CN), 64.2 (CH<sub>2</sub>), 41.6 (C), 1.16 (CH<sub>3</sub>) ppm. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -13 (NO<sub>2</sub>) - 134 (CN) ppm. <sup>109</sup>Ag ([D<sub>6</sub>]DMSO):  $\delta$  = 255 ppm. EA: Ag<sub>4</sub>C<sub>13</sub>H<sub>14</sub>N<sub>10</sub>O<sub>16</sub> (997.78): calc. C 15.65, H 1.41, N 14.04%. Found C 12.78, H 1.54, N 12.58%.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03540.

NMR spectra and vibrational data of salts; pictures of burning behavior tests with small-scale setup (PDF)

#### **Accession Codes**

CCDC 1850912 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Akhavan, J. *The Chemistry of Explosives*, 2nd. ed.; The Royal Society of Chemistry: Cambridge, 2004.

(2) Klapötke, T. M. Chemistry of High-Energy Materials, 4th ed.; de Gruyter: Berlin, 2017.

(3) Klapötke, T. M.; Krumm, B.; Ilg, R.; Troegel, D.; Tacke, R. The Sila-Explosives  $Si(CH_2N_3)_4$  and  $Si(CH_2ONO_2)_4$  Silicon Analogues of the Common Explosives Pentaerythrityl Tetraazide,  $C(CH_2N_3)_4$  and Pentaerythritol Tetranitrate,  $C(CH_2ONO_2)_4$ . J. Am. Chem. Soc. 2007, 129, 6908–6915.

(4) Axthammer, Q. J.; Klapötke, T. M.; Krumm, B.; Reith, T. Energetic Sila-Nitrocarbamates: Silicon Analogues of Neo-Pentane Derivatives. *Inorg. Chem.* **2016**, *55*, 4683–4692.

(5) Frankel, M. B. N-Nitrocarbamates. US2978485A, 1961.

(6) Aas, B.; Kettner, M. A.; Klapötke, T. M.; Sućeska, M.; Zoller, C. Asymmetric Carbamate Derivatives Containing Secondary Nitramine, 2,2,2-Trinitroethyl, and 2-Fluoro-2,2-dinitroethyl Moieties. *Eur. J. Inorg. Chem.* **2013**, 6028–6036.

(7) Axthammer, Q. J.; Klapötke, T. M.; Krumm, B.; Moll, R.; Rest, S. F. The Energetic Nitrocarbamate  $O_2NN(H)CO[OCH_2C(NO_2)_3]$ Derived from Phosgene. Z. Anorg. Allg. Chem. **2014**, 640, 76–83.

(8) Axthammer, Q. J.; Klapötke, T. M.; Krumm, B. Synthesis of Energetic Nitrocarbamates from Polynitro Alcohols and Their Potential as High Energetic Oxidizers. *J. Org. Chem.* 2015, 80, 6329–6335.

(9) Klapötke, T. M.; Krumm, B.; Reith, T. Polynitrocarbamates Derived from Nitromethane. Z. Anorg. Allg. Chem. 2017, 643, 1474– 1481.

(10) Gattow, G.; Knoth, W. K. Über Chalkogenolate. 119. Untersuchungen über N-Nitrocarbamate, N-Nitrocarbamidsäure-Oethylester und Salze dieses Esters. Versuche zur Darstellung von N-Nitrodithiocarbamaten. Z. Anorg. Allg. Chem. **1983**, 499, 194–204.

(11) Axthammer, Q. J.; Krumm, B.; Klapötke, T. M. Pentaerythritol-Based Energetic Materials Related to PETN. *Eur. J. Org. Chem.* **2015**, 723–729.

(12) Li, Y.; Huang, H.; Lin, X.; Pan, R.; Yang, J. Oxygen-rich Anion Based Energetic Salts with High Detonation Performances. *RSC Adv.* **2016**, *6*, 54310–54317.

(13) Li, Y.; Huang, H.; Yang, J. N-Nitrotrinitroethyl Carbamate Energetic Ionic Salts and Preparation Method and Application thereof. CN105777587 (A), 2016.

(14) Klapötke, T. M.; Witkowski, T. G.; Wilk, Z.; Hadzik, J. Determination of the Initiating Capability of Detonators Containing TKX 50, MAD X1, PETNC, DAAF, RDX, HMX or PETN as a Base Charge, by Underwater Explosion Test. *Propellants, Explos., Pyrotech.* **2016**, *41*, 92–97.

(15) Cotarca, L.; Eckert, H. *Phosgenations - A Handbook;* Wiley-VCH: Weinheim, 2005.

(16) Rasmussen, J. K.; Hassner, A. Recent Developments in the Synthetic Uses of Chlorosulfonyl Isocyanate. *Chem. Rev.* **1976**, *76*, 389–408.

(17) Graf, R. Über die Umsetzung von Chlorcyan mit Schwefeltrioxyd. Chem. Ber. **1956**, 89, 1071–1079.

(18) Dhar, D. N.; Dhar, P. The Chemistry of Chlorosulfonyl Isocyanate; World Scientific: Singapore, 2002.

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(19) Cox, B. G.; Natarajan, R.; Waghorne, W. E. Thermodynamic Properties for Transfer of Electrolytes from Water to Acetonitrile and to Acetonitrile + Water Mixtures. *J. Chem. Soc., Faraday Trans.* 1 1979, 75, 86–95.

(20) Guinand, L.; Hobt, K. L.; Mittermaier, E.; Rößler, E.; Schwenk, A.; Schneider, H. <sup>109</sup>Ag NMR-Study of the Selective Solvation of the Ag<sup>+</sup> Ion in Solvent Mixtures of Water and the Organic Solvents: Pyridine, Acetonitrile, Dimethyl Sulfoxide. *Z. Naturforsch., A: Phys. Sci.* **1984**, 39A, 83–94.

(21) Klapötke, T. M.; Krumm, B.; Moll, R.; Penger, A.; Sproll, S. M.; Berger, R. J. F.; Hayes, S. A.; Mitzel, N. W. Structures of Energetic Acetylene Derivatives  $HC \equiv CCH_2ONO_2$ ,  $(NO_2)_3CCH_2C \equiv CCH_2C$ - $(NO_2)_3$  and Trinitroethane,  $(NO_2)_3CCH_3$ . Z. Naturforsch., B: J. Chem. Sci. **2013**, 68B, 719–731.

(22) Sućeska, M. Explo5 V6.03; OZM Research, Zagreb, Croatia, 2015.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009. (24) Standardization Agreement 4489 (STANAG 4489), Explosives,

Impact Sensitivity Tests; NATO: Brussels, Belgium, 1999.

(25) Standardization Agreement 4487 (STANAG 4487), Explosives, Friction Sensitivity Tests; NATO: Brussels, Belgium, 2002.

(26) Council Regulation (EC) No. 440/2008 Laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Evaluation, Authorisation and Restriction of Chemicals (REACH); *Off. J. Eur. Communities: Legis.*, **2008**, Vol. 142, pp 93–103.

(27) Cao, C. J.; Johnson, M. S.; Hurley, M. M.; Klapötke, T. M. In Vitro Approach to Rapid Toxicity Assessment of Novel High-Nitrogen Energetics. *JANNAF J. Propuls. Energet.* **2012**, *5*, 41–51.

(28) Fischer, D.; Klapötke, T. M.; Reymann, M.; Stierstorfer, J. Dense Energetic Nitraminofurazanes. *Chem. - Eur. J.* 2014, 20, 6401–6411.

(29) Wasserbeschaffenheit - Bestimmung der Hemmwirkung von Wasserproben auf die Lichtemission von Vibrio Fischeri (Leuchtbakterientest); DIN EN ISO 11348-2, 2009.

(30) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. *SIR97*, 1997.

(31) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: a New Tool for Crystal Structure Determination and Refinement. J. Appl. Crystallogr. **1999**, *32*, 115–119.

(32) Sheldrick, G. M. SHELX-97, Programs for Crystal Structure Determination; University of Göttingen, Göttingen (Germany), 1997.
(33) Sheldrick, G. M. A. Short History of SHELX. Acta Crystallogr, Sect. A: Found. Crystallogr. 2008, 64A, 112–122.

(34) Farrugia, L. J. WinGX Suite for Small-molecule Single-crystal Crystallography. J. Appl. Crystallogr. **1999**, 32, 837–838.

(35) Spek, A. Structure Validation in Chemical Crystallography. *Acta Crystallogr.*, Sect. D: Biol. Crystallogr. **2009**, 65D, 148–155.

(36) Dennington, R. D., II; Keith, T. A.; Millam, J. M. *GaussView*, ver. 5.08; Semichem, Inc.: Wallingford, CT, 2009.

(37) Byrd, E. F. C.; Rice, B. M. Improved Prediction of Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations. J. Phys. Chem. A **2006**, 110, 1005–1013.

(38) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii. *Inorg. Chem.* **1999**, *38*, 3609–3620.

(39) Jenkins, H. D. B.; Tudela, D.; Glasser, L. Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements. *Inorg. Chem.* 2002, 41, 2364–2367.

(40) Jenkins, H. D. B.; Glasser, L. Ionic Hydrates,  $MpXq\cdot H_2O$ : Lattice Energy and Standard Enthalpy of Formation Estimation. *Inorg. Chem.* **2002**, *41*, 4378–4388.

(41) Jenkins, H. D. B. Chemical Thermodynamics at a Glance; Blackwell: Oxford, 2007.