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### Energetic salts based on nitroiminotetrazole-containing acetic acid<sup>†</sup>

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2-(5-Nitroiminotetrazol-1-yl)acetic acid (4) was synthesized from 100% nitric acid and ethyl 2-(5aminotetrazol-1-yl)acetate (2), which was easily obtained by reaction of ethyl aminoacetate hydrochloride, sodium hydroxide, and cyanogen azide. Compound 4 was also formed with 100% nitric acid and 2-(5-aminotetrazol-1-yl)acetic acid which was prepared from sodium 5-aminotetrazolate and 2-chloroacetic acid. New energetic materials comprised of nitroiminotetrazolate salts with nitroiminotetrazolate and carboxylate anions have been characterized spectroscopically as well as with single crystal X-ray diffraction and elemental analyses. In addition, the heats of formation ( $\Delta H_f$ ), and detonation pressures (*P*) and velocities (*D*) were calculated. All compounds were insensitive (>40 J) for impact with BAM Fallhammer.

### Introduction

In developing new energetic compounds, a number of factors come into play. Heats of formation, density, melting and decomposition temperatures, nitrogen content, and sensitivities should be considered. Previously known high energy density materials (HEDMs) are generally limited in one or more properties such as they are overly impact or friction sensitive, thermally unstable, difficult to synthesize on a large scale, not sufficiently energetic, or excessively hygroscopic. It is of course preferred that the high yield synthesis of an energetic compound be relatively simple and straightforward.

5-Aminotetrazoles, which are generally thermally stable and insensitive to impact, are one of the promising green HEDMs for generation of gases, as blowing agents, solid propellants, and thermally decomposing systems.<sup>1,2</sup> 5-Nitroiminotetrazoles, which can be prepared from 5-aminotetrazoles and 100% nitric acid,<sup>3</sup> as high nitrogen compounds are good candidates for high explosives because they combine both the strongly oxidizing nitroimino-group and the energetic nitrogen-rich backbone in one molecule (Scheme 1).<sup>4</sup>

Recently, the investigation of coloring agents for pyrotechnic compositions was focused on the new energetic materials for environmentally friendly compounds to the industrial applications.<sup>1b</sup> In 1969, Raap and Howard described the syntheses of several 5-aminotetrazolyl esters, which were obtained by alkylation of triethylammonium 5-aminotetrazolate with ethyl 2bromoacetate or methyl 2-chloroacetate.<sup>5</sup> The isomers that formed were separated by crystallization. Later, 1- or 2- alkylated 5-substituted tetrazoles were reported by the reaction of chloroacetic acid with sodium tetrazolate in water.6 The synthesis and structures of metal organic coordination compounds based on carboxylate-tetrazolate ligands were introduced with multifunctional ligands of both the carboxylate group and tetrazole group.7 The development of new HEDMs focuses on environmentally friendly compounds. To that end, the two different of anions (carboxylate and 5-nitroiminotetrazolate) could lead to interesting materials with new properties. We now report a new method to synthesize 2-(5-aminotetrazol-1-yl)acetic acid, using cyanogen azide with ethyl 2-aminoacetate, 2-(5-nitroiminotetrazol-1-yl)acetic acid, and its energetic salts.

### **Results and discussion**

Our interest in stable energetic materials containing 5-nitroiminotetrazole led to the investigation of the synthesis of 2-(5-nitroiminotetrazol-1-yl)acetic acid and its salts. The most



Scheme 1 Synthesis of 5-nitroiminotetrazoles.

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convenient route to 1-substituted 5-aminotetrazole is the addition of amine to cyanogen azide, which was found to be an efficient reagent for the synthesis of readily purified 1-substituted 5-aminotetrazoles from primary amines under non-catalytic conditions.<sup>2b,c</sup> Now we report that the primary amine, ethyl 2aminoacetate hydrochloride (1), serves for the synthesis of ethyl 2-(5-aminotetrazol-1-yl)acetate (2), which was achieved from the reaction of cyanogen azide with ethyl 2-aminoacetate (obtained by neutralization of 1 with sodium hydroxide) (Scheme 2). Cyanogen azide was obtained at 0 °C from cyanogen bromide and dry sodium azide in dry acetonitrile. Pure cyanogen azide is dangerous and toxic.<sup>8</sup>

Therefore, when utilizing the substance as a reactant, it must always be dissolved in a solvent to give a dilute solution. On the other hand, the alkylation of sodium 5-aminotetrazolate (3) using ethyl 2-bromoacetate was performed by following the literature procedure.<sup>5</sup> After recrystallization, our yield of **2** was 31%. At ambient temperature, nitration of **2** two times using 100% nitric acid without solvent has been shown to form 2-(5nitroiminotetrazol-1-yl)acetic acid (4). By nucleophilic substitution, **5** was also prepared from sodium 5-aminotetrazolate (3) and 2-chloroacetic acid. Nitration of **5** with 100% nitric acid led to **4** that was converted to the more stable energetic salts **6–11**. These salts were generally obtained by acid–base reactions between **4** and energetic bases in aqueous solutions. Next similar successful attempts were made to prepare bis(diaminoguanidinium) 2-(5-nitroiminotetrazol-1-yl)acetate (13) and bis(triaminoguanidinium) 2-(5-nitroiminotetrazol-1-yl) acetate (14) in good yields by metathesis with silver salt 12 (Scheme 2).

An attempt to nitrate **4** with a mixture of excess 100% nitric acid and 98% sulfuric acid to obtain 1-(dinitromethyl)-5-nitroiminotetrazole was unsuccessful since we were unable to isolate the compound from the reaction mixture by recrystallization (Scheme 3). When **4** was treated with excess 100% nitric acid and trifluoroacetic anhydride 2-(tetrazol-1-yl)acetic acid (**15**) was found resulting from the denitramination of **4** (Scheme 3). Compound **15** was characterized by single-crystal X-ray diffraction analysis (Fig. 1, Table 1).

2-(5-Nitroiminotetrazol-1-yl)acetic acid monohydrate  $(4 \cdot H_2O)$  crystallizes in the orthorhombic space group *Pbcn* with eight molecules per unit cell and a calculated density of 1.710 g cm<sup>-3</sup> (293(2) K) (Fig. 2, Table 1). The tetrazole ring of 4 is nearly planar [torsion angle N1–N2–N3–N4 0.67(13)°] and four similar bond lengths [N1–N2, N3–N4, N4–C5, C5–N1] are observed







Scheme 2 Synthesis and reactions of 2-(5-nitroiminotetrazol-1-yl)acetic acid (4).



Fig. 1 Single-crystal X-ray diffraction analysis of 15.

between 1.338(14) Å and 1.355(14) Å. The N2–N3 bond length of ring is 1.273(14) Å, which is a typical value observed for the nitroiminotetrazole.<sup>9</sup> The packing structure of  $4 \cdot H_2O$  is strongly influenced by strong hydrogen bonds between H<sub>2</sub>O and 4. These extensive hydrogen-bonding interactions between oxygen atom O1S from water and N4 [N4…O1S 2.651(13)] can be seen in Fig. 2b along the *c* axis.

Compound 9 crystallized in a triclinic cell in the space group  $P2_1/n$  with four molecules in the unit cell (Table 1). The tetrazole ring of 9 is nearly planar and four similar bond lengths are observed [N1–N2 1.344(18) Å, N3–N4 1.367(19) Å, N4–C5 1.331(19) Å, N1–C5 1.343(19) Å], and shows the delocalization of the negative charge from the ring (Fig. 3). The main change observed is the bond length of N2–N3 which corresponds to the N4 nitrogen atom that undergoes deprotonation in 4.

Table 1 Crystallographic data for 4 · H<sub>2</sub>O, 9, and 15

	$4\!\cdot\!\mathrm{H_2O}$	9	15
Chemical formula	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>5</sub>	C <sub>7</sub> H <sub>12</sub> N <sub>14</sub> O <sub>4</sub>	$C_3H_4N_4O_2$
Formula Mass	206.14	356.31	128.10
Crystal system	Orthorhombic	Monoclinic	Monoclinic
a/Å	23.1690(14)	5.4438(8)	12.4884(7)
b/Å	8.6022(5)	16.020(2)	5.0947(3)
c/Å	8.0337(5)	17.071(3)	17.4942(10)
α (°)	90	90	90
β(°)	90	92.374(2)	99.941(1)
γ (°)	90	90	90
Unit cell volume/Å <sup>3</sup>	1601.15(17)	1487.5(4)	1096.35(11)
T/K	293(2)	296(2)	293(2)
Space group	Pbcn	$P2_1/n$	$P2_1/c$
No. of formula units	8	4	8
per unit cell, $Z$			
Radiation type	Μο-Κα	Μο-Κα	Μο-Κα
Absorption coefficient,	0.159	0.132	0.132
$\mu/\text{mm}^{-1}$			
Density <sub>calcd</sub> /g cm <sup>-3</sup>	1.710	1.591	1.552
No. of reflections	16419	12677	8688
measured			
No. of independent	1996	2842	2252
reflections			
R <sub>int</sub>	0.0199	0.0241	0.0200
Final $R_1$ values	0.0332	0.0354	0.0332
$(I > 2\sigma(I))^a$			
Final $wR_2$ values	0.0927	0.0890	0.0835
$(I > 2\sigma(I))^{b}$			
Final $R_1$ values	0.0360	0.0486	0.0416
(all data)			
Final $wR_2$ values	0.0954	0.0968	0.0891
(all data)			
Goodness of fit on $F^2$	1.032	1.051	1.032
CCDC number <sup>c</sup>	861469	861471	861470
CCD C humovi	001107	0011/1	0011/0

<sup>*a*</sup>  $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ . <sup>*b*</sup>  $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}$ . <sup>*c*</sup> CCDC numbers contain the supplementary crystallographic data for this paper (see ESI). Deprotonation results in a lengthening of the N1–N2, N3–N4, C5–N10 distances between  $\sim 0.01$  Å and  $\sim 0.03$  Å. These distances are considerably longer than N2–N3 double bonds [1.285(2) Å] but significantly shorter than the N1–C1 [1.443(18) Å] single bond. C7–O8 and C7–C9 bond lengths of the deprotonated carboxyl group observed at 1.224 Å and 1,265 Å, respectively. A weak intermolecular hydrogen bond is found between the atoms N19A and O8 [N19A–H19A···O8 3.230(3) Å]. The triazole ring proton forms a very strong hydrogen bond to the carboxylate anion [N17A–H17A···O9 2.537(19) Å].

The <sup>15</sup>N NMR spectra of 2-(5-nitroiminotetrazol-1-yl)acetic acid and its salts were measured in DMSO[D<sub>6</sub>] solution and chemical shifts are given with respect to CH<sub>3</sub>NO<sub>2</sub> as external standard (Fig. 4). The signal at the highest field for energetic salts can be easily assigned as the amino group (NH, NH<sub>2</sub>) nitrogen atom resonance.<sup>9d,2d</sup> In the case of salts **6**, **10** and **14** the position of N1 is observed at lower field (~80 ppm) than that of the nitroiminotetrazole **4**.

Calculations of heats of formation, which is one of the important characteristics for energetic salts, were performed by using the Gaussian 03 (Revision D.01) program. The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the  $6-31+G^{**}$  basis set, and single-point energies were calculated at the MP2/ $6-311++G^{**}$ 



**Fig. 2** Single-crystal X-ray diffraction analysis of  $4 \cdot H_2O$ .



Fig. 3 Single-crystal X-ray diffraction analysis of 9.

level. All of the energetic materials exhibit positive heats of formation (except 5,  $-0.68 \text{ kJ g}^{-1}$ ) with 4 and 11 having the highest at 2.11 and 2.08 kJ g<sup>-1</sup>, respectively (Table 2). The thermal stabilities of all compounds were studied with differential scanning calorimetry (DSC) at a heating rate of 10 °C min<sup>-1</sup>. Eight compounds (6–11, 13, 14) melt before decomposing and only 4 was decomposed at 162 °C (Table 2). Compounds 7 and 9 melt at 92 °C and 93 °C, respectively, which suggest definition as ionic liquids. Compound 6 has the highest thermal stability to 255 °C.

Densities for these compounds were found in the range between 1.498 and 1.671 g cm<sup>-3</sup> with a gas pycnometer (Table 2) (TNT: 1.65 g cm<sup>-3</sup>). By using the experimental values for the densities of **4** and energetic salts (**6–11**, **13**, **14**), the detonation pressures (*P*) and velocities (*D*) were calculated based on traditional Chapman-Jouget thermodynamic detonation theory using Cheetah 5.0.<sup>11</sup> For compounds (**6–11**, **13**, **14**), the calculated detonation pressures lie in the range between 20.11 and 25.75 GPa (TNT: 19.5 GPa). Detonation velocities are found in the range between 7369 and 8344 m s<sup>-1</sup> (TNT: 6881 m s<sup>-1</sup>). For initial safety testing, the impact sensitivity was determined according to BAM methods (BAM Fallhammer).<sup>12</sup> All of the compounds are insensitive toward impact with sensitivities more than 40 J (TNT: 15 J).

### Conclusions

2-(5-Aminotetrazol-1-yl)ethyl ester was synthesized by reaction of ethyl 2-aminoacetate (1) and cyanogen azide or by nucleophilic substitution of sodium 5-aminotetrazolate (3) and ethyl 2-bromoacetate. The target compound of 2-(5-nitroiminotetrazol-1-yl)acetic acid (4), obtained from 2 and 100% nitric acid, and the corresponding salts 6-11, 13, and 14 were synthesized and fully characterized by means of IR, <sup>1</sup>H-, <sup>13</sup>C-, <sup>15</sup>N-NMR spectroscopy, and elemental analysis as well as singlecrystal X-ray diffraction analysis. Compound 4 could be prepared also from 2-(5-aminotetrazol-1-yl)acetic acid (5) with 100% nitric acid in 98% yield. Structures of 4 · H<sub>2</sub>O, 9 and 15 are supported by single crystal X-ray analyses. The thermal behavior of compound 4 and its salts was investigated by DSC measurements. Compound 4 decomposed at 162 °C with its more thermally stable salts decomposing in the range between 181 and 255 °C. Furthermore, they are all impact insensitive energetic materials with good calculated detonation properties for environmentally friendly explosive applications.

### **Experimental section**

### Safety precautions

While we have experienced no difficulties with the impact instability of all compounds, manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn. Extreme caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided.

### General methods

<sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) and 500 MHz (Bruker AVANCE 500) Nuclear Magnetic Resonance spectrometers operating at 300.13, 75.48 and 50.69 MHz, respectively, by using DMSO[D<sub>6</sub>] as solvent and locking solvent unless otherwise stated. The melting and decomposition points were obtained on a Differential Scanning Calorimeter (TA Instruments Company, Model: Q10) at a scan rate of 10 °C min<sup>-1</sup>. IR spectra were recorded using KBr pellets for solids on BIORAD model 3000 FTS spectrometer. Densities of the nitroiminotetrazole and its salts were determined at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer. Details of the X-ray diffraction analysis of compounds 4 · H<sub>2</sub>O, 9, and 15 are provided. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART PLATINUM 135 CCD detector.<sup>13-17</sup>

#### Theoretical study

Calculations were carried out by using the Gaussian 03 (Revision D.01) suite of programs.<sup>18</sup> The geometric optimization of the



Fig. 4 <sup>15</sup>N NMR spectra of 4, 6, 10, 11, and 14.

structures and frequency analyses were carried out by using the B3-LYP functional with the  $6-31+G^{**}$  basis set,<sup>19</sup> and singlepoint energies were calculated at the MP2/6-311++G<sup>\*\*</sup> level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on Born-Haber energy cycles (Fig. 5), heats of formation of ionic salts can be simplified by the formula [eqn (1)]:

$$\Delta H_{\rm f}^{\circ} \text{ (ionic salt, 298 K)} = \Delta H_{\rm f}^{\circ} \text{ (cation, 298 K)} + \Delta H_{\rm f}^{\circ} \text{ (anion, 298 K)} - \Delta H_{\rm L}$$
(1)

where  $\Delta H_{\rm L}$  is the lattice energy of the ionic salt. The  $\Delta H_{\rm L}$  value could be predicted by the formula suggested by Jenkins *et al.* [eqn (2)],<sup>20</sup> where  $U_{\rm POT}$  is the lattice potential energy and  $n_{\rm M}$  and  $n_{\rm X}$ 

depend on the nature of the ions  $M_p^+$  and  $X_q^-$ , respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_{\rm L} = U_{\rm POT} + [p(n_{\rm M}/2 - 2) + q(n_{\rm X}/2 - 2)]RT$$
(2)

The equation for the lattice potential energy,  $U_{POT}$ , takes the form of eqn (3),

$$U_{\rm POT} \,({\rm kJ} \,\,{\rm mol}^{-1}) = \gamma (\rho_{\rm m}/M_{\rm m})^{1/3} + \delta$$
 (3)

where  $\rho_{\rm m}$  is the density (g cm<sup>-3</sup>), M<sub>m</sub> is the chemical formula mass of the ionic material (g), and the coefficients  $\gamma$  (kJ mol<sup>-1</sup> cm) and  $\delta$  (kJ mol<sup>-1</sup>) are assigned literature values.<sup>19</sup>

Table 2 Physical properties of energetic salts

Compd	$T_{\rm m}^{\ a}$ (°C)	$T_{\rm dec}{}^a$ (°C)	density <sup>b</sup> (g cm <sup><math>-3</math></sup> )	$\Delta H_{\rm f}^{\circ c}$ (kJ mol <sup>-1</sup> )	$\Delta H_{\rm f}^{\circc}~({\rm kJ}~{\rm g}^{-1})$	$P^d$ (GPa)	$\nu D^e \text{ (m s}^{-1}\text{)}$	$\mathrm{IS}^{f}(\mathrm{J})$
4	_	162	1.671	513.3	2.11	25.28	7918	>40
6	241	255	1.541	-151.5	-0.68	20.30	7682	>40
7	92	201	1.567	193.3	0.77	25.08	8344	>40
8	205	211	1.567	429.8	1.21	20.11	7369	>40
9	93	187	1.542	700.7	1.97	21.74	7492	>40
10	228	232	1.645	378.4	0.98	$20.87^{h}$	$7806^{h}$	>40
11	162	181	1.665	746.5	2.08	25.75	8303	>40
13	140	187	1.498	391.7	1.07	21.52	7925	>40
14	170	181	1.529	622.5	1.57	24.07	8316	>40
$TNT^{g}$	80	295	1.65	-295.0	-1.38	19.5	6881	15

<sup>*a*</sup> Melting and thermal decomposition temperature under nitrogen gas (DSC, 10 °C min<sup>-1</sup>). <sup>*b*</sup> Gas pycnometer (25 °C). <sup>*c*</sup> Heat of formation (calculated via Gaussian 03). <sup>*d*</sup> Calculated detonation pressure (Cheetah 5.0). <sup>*e*</sup> Calculated detonation velocity (Cheetah 5.0). <sup>*f*</sup> Impact sensitivity (BAM drophammer). <sup>*g*</sup> Ref. 10. <sup>*h*</sup> Cheetah 4.0.



Fig. 5 Born-Haber cycle for the formation of nitroiminotetrazolate salts.

The remaining task is to determine the heats of formation of the cations and anions, which are computed by using the method of isodesmic reactions (see ESI). The enthalpy of an isodesmic reaction  $(\Delta H_{r298}^{\circ})$  is obtained by combining the MP2/6-311++G\*\* energy difference for the reaction, the scaled zeropoint energies (B3LYP/6-31+G\*\*), and other thermal factors (B3LYP/6-31+G\*\*). Thus, the heats of formation of the cations and anions being investigated can be extracted readily (see ESI). With the value of the heats of formation and density of the energetic salts, the detonation pressures (*P*) and detonation velocities (v*D*) were calculated based on the traditional Chapman-Jouget thermodynamic detonation theory by using Cheetah 5.0.<sup>11</sup>

### **Compound synthesis**

### Ethyl 2-(5-aminotetrazol-1-yl)acetate (2)

**Method A.** At 0 °C, 10.0 g (94.3 mmol) cyanogen bromide was dissolved in 120 mL dry acetonitrile to which was added 36.5 g (0.562 mol) dry sodium azide. The reaction mixture was stirred at 0 °C for 4 h. The inorganic salt was removed by filtration (after filtering, the salt must be dissolved in cold water quickly). Ethyl aminoacetate hydrochloride (4.00 g, 28.7 mmol) required 1.15 g (0.0287 mol) sodium hydroxide for the neutralization in 20 mL water at 0 °C. The cyanogen azide solution is added to the solution containing ethyl aminoacetate below 0 °C. After stirring overnight at ambient temperature, the solvent was removed by blowing air over the liquid surface. The product was purified by washing with water and acetonitrile. White solid  $2^5$  was obtained in a yield of 71% (3.50 g, 20.4 mmol).

White solid; mp 151 °C.  $\tilde{\nu}$ /cm<sup>-1</sup> 3368, 3266, 3164, 2999, 2961, 2907, 2787, 2741, 1744, 1651, 1591, 1492, 1376, 1296, 1270, 1229, 1126, 1098, 1024, 878, 806, 758.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 1.21 (3 H, t), 4.17 (2 H, q), 5.10 (2 H, s), 6.80 (2 H, s, NH<sub>2</sub>).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 13.9, 61.5, 156.1, 166.6. Found: C, 34.93; H, 5.25; N, 41.19. Calc. for C<sub>5</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>: C, 35.09; H, 5.30; N, 40.92.

**Method B.** Compound **2** was prepared using the same process given in the literature<sup>5</sup> with 12.4 g (0.146 mol) 5-aminotetrazole, 24.4 g (0.146 mol) 2-bromoacetate, 14.8 g (0.146 mol) triethylamine, and 50 mL acetone. White solid **2** was obtained in a yield of 31% (7.74 g, 45.2 mmol).

#### 2-(5-Nitroiminotetrazol-1-yl)acetic acid monohydrate (4·H<sub>2</sub>O)

Method A. At 0 °C, 14.0 g (81.8 mmol) ethyl 2-(5-aminotetrazol-1-yl)acetate (2) was added in small portions to 25 mL 100% HNO<sub>3</sub>. The reaction mixture was stirred at ambient temperature for 18 h. The solution was poured into *ca*. 100 g ice. After removing water by blowing air over the liquid surface, the white solid was added to 25 mL 100% HNO<sub>3</sub> at 0 °C. The reaction mixture was stirred at ambient temperature for 18 h. The solution was poured into *ca*. 100 g ice. The solvent was removed by blowing air over the liquid surface. The product was purified by washing with water. White solid  $4 \cdot H_2O$  was obtained in a yield of 65% (11.0 g, 53.4 mmol). The water of crystallization of  $4 \cdot H_2O$  could be removed under high vacuum at 60 °C for 5 h.  $4 \cdot H_2O$  was obtained upon recrystallization from water.

Method B. At 0 °C, 15.0 g (0.105 mol) 2-(5-aminotetrazol-1-yl) acetic acid (5)<sup>6</sup> was added in small portions to 24 mL 100% HNO<sub>3</sub>. The reaction mixture was stirred at ambient temperature for 20 h. The solution was poured into *ca*. 100 g ice. The solvent was removed by blowing air over the liquid surface. The product was purified by washing with water. White solid  $4 \cdot H_2O$  was obtained in a yield of 98% (21.1 g, 0.102 mol).). Colorless crystal; mp 96 °C (H<sub>2</sub>O), 164 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3397, 3202, 3140, 3031, 2975, 1751, 1584, 1510, 1462, 1437, 1402, 1320, 1250, 1204, 1041, 993, 948, 899, 797, 777, 716, 650.  $\delta_{\rm H}$  (300 MHz, DMSO[D<sub>6</sub>]) 5.12 (2 H, s, CH<sub>2</sub>), 7.52 (4 H, br s).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 47.8, 150.4, 167.2. Found C, 18.03; H, 2.24; N, 42.29. Calc. for C<sub>3</sub>H<sub>4</sub>N<sub>6</sub>O<sub>4</sub>·0.5H<sub>2</sub>O: C, 18.28; H, 2.56; N, 42.64. Density = 1.710 g cm<sup>-3</sup>. Impact sensitivity >40 J.

**4.** White solid; mp 162 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3401, 3214, 3142, 3031, 2974, 1751, 1586, 1511, 1465, 1438, 1401, 1321, 1250, 1206, 1041, 996, 948, 903, 797, 778, 745, 716, 652.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 5.11 (2 H, s, CH<sub>2</sub>), 13.76 (2 H, s).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 47.2, 150.5, 167.0.  $\delta_{14\rm N}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -15.7 (NO<sub>2</sub>).  $\delta_{15\rm N}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -172.8, -155.6, -153.2, -23.3, -15.7.  $\delta_{\rm H}$  (300 MHz; D<sub>2</sub>O) 5.17 (2 H, s, CH<sub>2</sub>).  $\delta_{\rm C}$  (75.5 MHz; D<sub>2</sub>O) 47.2, 168.3. Found C, 19.18; H, 2.10; N, 44.77. Calc. for C<sub>3</sub>H<sub>4</sub>N<sub>6</sub>O<sub>4</sub>: C, 19.16; H, 2.14; N, 44.68. Density: 1.671 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

### Bi(ammonium) 4-(carboxylatomethyl)-5-nitroiminotetrazolate hydrate $(6 \cdot H_2O)$

The reaction of 220 mg (1.07 mmol) 2-(5-nitroiminotetrazol-1-yl) acetic acid monohydrate ( $4 \cdot H_2O$ ) with 28 – 30% excess aqueous ammonia in 10 mL water at ambient temperature for 10 min gave white solid  $6 \cdot H_2O$  (230 mg, 0.958 mmol, 89%) after air drying. White solid; mp 143 °C ( $H_2O$ ), 244 °C, 254 °C (dec.).  $\tilde{\nu}/cm^{-1}$  3443, 3180, 2997, 2856, 1598, 1513, 1468, 1431, 1387, 1319, 1293, 1260, 1148, 1108, 1036, 892, 797, 741, 682.  $\delta_H$  (300 MHz; DMSO [D<sub>6</sub>]) 4.45 (2 H, s, CH<sub>2</sub>), 6.82 (10 H, br. s, <sup>+</sup>NH<sub>4</sub> and H<sub>2</sub>O).  $\delta_C$  (75.5 MHz; DMSO[D<sub>6</sub>]) 49.4, 156.8, 169.1. Found C, 15.20; H, 5.22; N, 46.47. Calc. for C<sub>3</sub>H<sub>12</sub>N<sub>8</sub>O<sub>5</sub>: C, 15.00; H, 5.04; N, 46.65. Density: 1.563 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

The water of crystallization of  $\mathbf{6} \cdot H_2O$  was removed under high vacuum at 60 °C for 5 h.

**6.** White solid; mp 241 °C, 255 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3397, 3208, 2851, 1684, 1598, 1511, 1436, 1381, 1336, 197, 1260, 1108, 797, 739, 704, 683.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 4.49 (2 H, s, CH<sub>2</sub>), 7.39 (8 H, s, <sup>+</sup>NH<sub>4</sub>).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 49.3, 156.8, 169.2.

 $\delta_{15N}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -345.7, -149.5, -143.5, -63.4, -7.0, -2.9, 14.6. Found C, 16.51; H, 4.37; N, 49.82. Calc. for C<sub>3</sub>H<sub>10</sub>N<sub>8</sub>O<sub>4</sub>: C, 16.22; H, 4.54; N, 50.44. Density: 1.541 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

## Bi(hydrazinium) 4-(carboxylatomethyl)-5-nitroiminotetrazolate (7)

The reaction of 250 mg (1.21 mmol) 2-(5-nitroiminotetrazol-1-yl) acetic acid monohydrate (**4**·H<sub>2</sub>O) with 0.02 mL 98% hydrazine hydrate in 6 mL water at ambient temperature for 10 min gave white solid 7 (285 mg, 1.19 mmol, 98%) after air drying. White solid; mp 92 °C, 201 °C (dec.).  $\bar{\nu}/\text{cm}^{-1}$  3441, 3325, 3158, 3115, 3005, 2962, 2748, 1655, 1614, 1584, 1509, 1458, 1387, 1342, 1310, 1104, 1088, 961, 798.  $\delta_{\text{H}}$  (300 MHz; DMSO[D<sub>6</sub>]) 4.52 (2 H, s, CH<sub>2</sub>), 6.62 (10 H, s).  $\delta_{\text{C}}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 49.4, 156.8, 169.9.  $\delta_{15N}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -332.7, -162.6, -156.9, -75.9, -20.1, -16.0, 1.7. Found C, 13.55; H, 4.83; N, 53.00. Calc. for C<sub>3</sub>H<sub>12</sub>N<sub>10</sub>O<sub>4</sub>·0.5H<sub>2</sub>O: C, 13.79; H, 5.02; N, 53.62. Density: 1.567 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

### Bis(3-amino-1,2,4-triazolium) 4-(carboxylatomethyl)-5nitroiminotetrazolate (8)

The reaction of 350 mg (1.86 mmol) 2-(5-nitroiminotetrazol-1-yl) acetic acid (**4**) with 313 mg (3.72 mmol) 3-amino-1,2,4-triazole in 10 mL water at ambient temperature for 10 min gave white solid **8** (620 mg, 1.74 mmol, 94%) after air drying. White solid; mp 205 °C, 211 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3393, 3318, 3261, 3158, 3013, 2749, 1686, 1626, 1609, 1517, 1462, 1382, 1340, 1303, 1267, 1111, 1037, 950, 891, 801, 700, 682.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 4.89 (2 H, s, CH<sub>2</sub>), 7.90 (2 H, s), 8.76 (8 H, br. s).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 47.0, 143.3, 154.4, 157.2, 168.6.  $\delta_{15N}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -327.3, -205.0, -198.4 - 169.2, -157.3, -115.6, -78.5, -20.9, -15.6, 3.1. Found C, 23.28; H, 3.45; N, 54.57. Calc. for C<sub>7</sub>H<sub>12</sub>N<sub>14</sub>O<sub>4</sub>: C, 23.60; H, 3.40; N, 55.04. Density: 1.567 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

### Bis(4-amino-1,2,4-triazolium) 4-(carboxylatomethyl)-5nitroiminotetrazolate (9)

The reaction of 350 mg (1.86 mmol) 2-(5-nitroiminotetrazol-1-yl) acetic acid (**4**) with 313 mg (3.72 mmol) 4-amino-1,2,4-triazole in 10 mL water at ambient temperature for 10 min gave white solid **8** (600 mg, 1.68 mmol, 91%) after air drying. Colorless crystal; mp 93 °C, 195 °C (dec.).  $\tilde{\nu}/\text{cm}^{-1}$  3429, 3358, 3274, 3103, 2852, 1682, 1624, 1513, 1463, 1389, 1341, 1296, 1204, 1150, 1111, 1078, 1038, 992, 621.  $\delta_{\text{H}}$  (300 MHz; DMSO[D<sub>6</sub>]) 5.00 (2 H, s, CH<sub>2</sub>), 8.55 (6 H, s), 8.91 (4 H, s);  $\delta_{\text{C}}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 47.2, 144.6, 156.8, 168.5.  $\delta_{15\text{N}}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -311.8, -193.6, -171.0, -157.6, -92.0, -86.0, -21.8, -15.9, 0.8. Found C, 23.70; H, 3.58; N, 55.23. Calc. for C<sub>4</sub>H<sub>12</sub>N<sub>14</sub>O<sub>4</sub>: C, 23.60; H, 3.40; N, 55.04. Density: 1.542 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

### Bis(3,5-diamino-1,2,4-triazolium) 4-(carboxylatomethyl)-5nitroiminotetrazolate (10·2H<sub>2</sub>O)

The reaction of 380 mg (2.02 mmol) 2-(5-nitroiminotetrazol-1-yl) acetic acid (4) with 400 mg (4.04 mmol) 3,5-diamino-1,2,4-triazole in 5 mL water at ambient temperature for 10 min stirring precipitated a white solid, which was filtered, washed with water and dried. **10** was obtained in a yield of 77% (655 mg, 1.55 mmol). White solid; mp 95 °C (H<sub>2</sub>O), 232 °C, 235 °C (dec.);  $\tilde{\nu}/\text{cm}^{-1}$  3460, 3418, 3349, 3192, 2923, 2655, 1725, 1686, 1655, 1530, 1511, 1457, 1397, 1326, 1291, 1268,1117, 797, 729, 701. Found C, 19.96; H, 4.17; N, 53.29. Calc. for C<sub>7</sub>H<sub>14</sub>N<sub>16</sub>O<sub>4</sub> · 2H<sub>2</sub>O: C, 19.91; H, 4.30; N, 53.07.

The water of crystallization of  $10 \cdot 2H_2O$  could be removed under high vacuum at 60 °C for 5 h.

**10.** White solid; mp 228 °C, 232 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3422, 3349, 3201, 3178, 2922, 2805, 2743, 1695, 1662, 1624, 1602, 1537, 1514, 1461, 1384, 1341, 1303, 1267, 1115, 1048, 999, 888, 860, 801, 728, 702.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 4.77 (2 H, s, CH<sub>2</sub>), 7.29 (12 H, br. s).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 477, (2 H, s, CH<sub>2</sub>), 7.29 (12 H, br. (50.7 MHz; DMSO[D<sub>6</sub>]) -328.4, -227.6, -196.3, -166.3, -156.2, -75.5, -19.4, -14.7, 4.0. Found C, 21.39; H, 3.65; N, 56.71. Calc. for C<sub>7</sub>H<sub>14</sub>N<sub>16</sub>O<sub>4</sub>·0.5H<sub>2</sub>O: C, 21.27; H, 3.82; N, 56.69. Density: 1.645 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

### Bis(5-aminotetrazolium) 4-(carboxylatomethyl)-5nitroiminotetrazolate (11)

The reaction of 370 mg (1.97 mmol) 2-(5-nitroiminotetrazol-1-yl) acetic acid (4) with 406 mg (3.94 mmol) 5-aminotetrazole monohydrate in 30 mL acetonitrile under reflux for 12 h refluxing precipitated a white solid, which was filtered, washed with acetonitrile and dried. **11** was obtained in a yield of 89% (630 mg, 1.76 mmol). White solid; mp 164 °C, 182 °C (dec.).  $\bar{\nu}/\text{cm}^{-1}$  3447, 3352, 3227, 2959, 2925, 2853, 2761, 2651, 2541, 1709, 1692, 1649, 1510, 1462, 1402, 1337, 1310, 1289, 1249, 1194, 1067, 1034, 797, 737.  $\delta_{\text{H}}$  (300 MHz; DMSO[D<sub>6</sub>]) 5.09 (2 H, s, CH<sub>2</sub>), 10.07 (6 H, br. s), 16.64 (2 H, br. s).  $\delta_{\text{C}}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 47.7, 151.4, 156.5, 167.3.  $\delta_{14\text{N}}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -17.9 (NO<sub>2</sub>).  $\delta_{15\text{N}}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -337.5, -175.0, -158.3, -143.8, -138.9, -25.5, -21.5, -18.2, -12.9. Found C, 16.70; H, 2.72; N, 62.30. Calcd for C<sub>5</sub>H<sub>10</sub>N<sub>16</sub>O<sub>4</sub>: C, 16.76; H, 2.81; N, 62.56. Density: 1.665 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

### Silver 4-(carboxylatomethyl)-5-nitroiminotetrazolate (12)

Silver nitrate (4.04 g, 23.8 mmol) was dissolved in 20 mL of water and added to a solution of sodium 2-(5-nitroiminotetrazol-1-yl) acetate, which was obtained from 2.46 g (11.9 mmol) 2-(5nitroiminotetrazol-1-yl)acetic acid monohydrate ( $4 \cdot H_2O$ ) and 0.952 g (23.8 mmol) sodium hydroxide in 35 mL of water. The silver salt precipitated immediately as a white powder. The suspension was stirred for five hours at ambient temperature. The product was filtered off and dried with air overnight. Gray solid **12** was obtained in a yield of 91% (4.35 g, 10.8 mmol). Gray solid; mp 275 °C (dec.).  $\tilde{\nu}/cm^{-1}$  3431, 3011, 2958, 1631, 1584, 1500, 1455, 1377, 1348, 1324, 1273, 1238, 1185, 1148, 1108, 1037, 885, 795, 687.

### Bis(diaminoguanidinium) 4-(carboxylatomethyl)-5nitroiminotetrazolate (13)

To an aqueous solution of 625 mg (4.98 mmol) diaminoguanidine hydrochloride in 10 mL of water was added 1.00 g (2.49 mmol) silver 4-(carboxylatomethyl)-5-nitroiminotetrazol-1-ide (12).

After stirring at ambient temperature for 3 h, the silver salt was removed by filtering the solution three times, and the solvent was removed under a stream of air. A 0.890 g portion (2.43 mmol, 98%) of colorless crystal **13** was obtained. Colorless crystal; mp 140 °C, 213 °C (dec.).  $\bar{\nu}/cm^{-1}$  3386, 3331, 3303, 3252, 3150, 3068, 1678, 1636, 1505, 1454, 1393, 1339, 1295, 1261, 1187, 1157, 1111, 1038, 978, 889, 801, 707, 591.  $\delta_{\rm H}$  (300 MHz; D<sub>2</sub>O) 4.97 (2 H, s, CH<sub>2</sub>), 7.09 (4 H, br. s), 8.47 (4 H, br. s).  $\delta_{\rm C}$  (75.5 MHz; D<sub>2</sub>O) 49.0, 155.9, 159.8, 172.2.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 4.53 (10 H, s, NH<sub>2</sub> and CH<sub>2</sub> overlap), 7.41 (4 H, s), 9.20 (4 H, s).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 49.3, 156.9, 160.3, 170.5.  $\delta_{\rm 14N}$  (50.7 MHz; DMSO [D<sub>6</sub>]) -14.5 (NO<sub>2</sub>).  $\delta_{\rm 15N}$  (50.7 MHz; DMSO[D<sub>6</sub>]) -327.4, -311.6, -287.0, -161.7, -155.9, -73.6, -18.9, -15.0 (NO<sub>2</sub>), 2.9. Found C, 15.89; H, 4.85; N, 60.71. Calc. for C<sub>5</sub>H<sub>18</sub>N<sub>16</sub>O<sub>4</sub>: C, 16.39; H, 4.95; N, 61.18. Density: 1.498 g cm<sup>-3</sup>, Impact sensitivity: >40 J.

### Bis(triaminoguanidinium) 4-(carboxylatomethyl)-5nitroiminotetrazolate monohydrate (14·H<sub>2</sub>O)

To an aqueous solution of 700 mg (4.98 mmol) triaminoguanidine hydrochloride in 10 mL of water was added 1.00 g (2.49 mmol) silver 4-(carboxylatomethyl)-5-nitroiminotetrazol-1-ide (**12**). After stirring at ambient temperature for 3 h, the silver salt was removed by filtering 3 times, and the solvent was removed under air. A 0.880 g portion (2.22 mmol, 89%) of white solid **14**·H<sub>2</sub>O was obtained. White solid; mp 109 °C (H<sub>2</sub>O), 170 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3625, 3351, 3294, 3264, 3215, 1683, 1611, 1504, 1443, 1377, 1327, 1293, 1244, 1131, 1103, 1038, 1009, 951, 913, 795, 678, 637, 558.  $\delta_{\rm H}$  (300 MHz; D<sub>2</sub>O) 4.99 (2 H, s, CH<sub>2</sub>), 8.55 (br. s).  $\delta_{\rm C}$  (75.5 MHz; D<sub>2</sub>O) 48.9, 155.8, 159.2, 172.1.  $\delta_{\rm 15N}$ (50.7 MHz; D<sub>2</sub>O) -323.6, -281.2, -154.1, -147.1, -73.3, -13.6, -8.3, 3.7. Found C, 14.17; H, 5.41; N, 61.06. Calc. for C<sub>5</sub>H<sub>22</sub>N<sub>18</sub>O<sub>5</sub>·H<sub>2</sub>O: C, 14.49; H, 5.35; N, 60.85.

The water of crystallization of  $14 \cdot H_2O$  could be removed by heating under high vacuum at 60 °C for 5 h.

**14.** White solid; mp 170 °C, 188 °C (dec.).  $\tilde{\nu}$ /cm<sup>-1</sup> 3348, 3322, 3212, 3003, 2954, 1686, 1615, 1505, 1458, 1384, 1340, 1300, 1256, 1204, 1133, 1112, 1036, 972, 893, 801, 682, 637, 611.  $\delta_{\rm H}$  (300 MHz; DMSO[D<sub>6</sub>]) 4.47 (14 H, s, NH<sub>2</sub> and CH<sub>2</sub> overlap), 8.65 (6 H, br. s).  $\delta_{\rm C}$  (75.5 MHz; DMSO[D<sub>6</sub>]) 49.7, 156.9, 159.3, 169.0. Found C, 14.87; H, 5.14; N, 62.15. Calc. for C<sub>5</sub>H<sub>20</sub>N<sub>18</sub>O<sub>4</sub>: C, 15.15; H, 5.09; N, 63.61. Density: 1.529 g cm<sup>-3</sup>. Impact sensitivity: >40 J.

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