Nitrogen-Rich Salts of 1-Methyl-5-nitriminotetrazolate: An Auspicious Class of Thermally Stable Energetic Materials

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1-Methyl-5-nitriminotetrazole (**1**) was formed by nitration of 1-methyl-5-aminotetrazole, which was obtained by methylation of sodium 5-aminotetrazolate. **1** was deprotonated using potassium hydroxide forming the corresponding potassium salt (**2**), which was transformed into silver 1-methyl-5-nitriminotetrazolate (**3**) by the reaction with silver nitrate. Guanidinium (**4**), 1-aminoguanidinium (**5**), 1,3-diaminoguanidinium (**6**), 1,3,5-triaminoguanidinium (**7**), and azidoformamidinium (**8**) 1-methyl-5-nitriminotetrazolate were prepared by metathesis reactions either using **2** and guanidinium perchlorates or **3** and guanidinium chlorides under the precipitation of $KClO_4$ or AgCl, respectively. All compounds were fully characterized by single crystal X-ray diffraction, vibrational spectroscopy, multinuclear NMR spectroscopy, elemental analysis, differential scanning calorimetry (DSC) as well as bomb calorimetry. Since the packing of molecules in the solid state influences the properties of materials significantly, a detailed description of the crystal structures of **3**, **4**, **6**, **7**, and **8** is given. Using the heats of combustion the heats of formations were calculated to be strongly endothermic. Several detonation parameters like the detonation pressure and detonation velocity were calculated using the EXPLO5 software. In addition the sensitivities were tested using the BAM drop hammer and friction tester. With respect to developing new high explosives triaminoguanidinium 1-methyl-5-nitriminotetrazolate shows the most promising values and was therefore successfully tested in a Koenen Test (critical diameter ≤ 10 mm).

Introduction

The development of high-energy-density materials (HEDM)[1] is an ongoing area of interest in our research group.[2] Generally the class of HEDMs is divided into two main groups, according to their different applications in military and civil sectors. These main groups are explosives and propellants. Due to their qualification profile the materials have to meet specific characteristics. Important criteria for the group of explosives are the detonation velocity v_D and the detonation pressure p_D. Thereby the focus lies on the synthesis of compounds, which feature values as high as possible for both magnitudes, to reach maximum performance. Another critical parameter is the density ρ of the explosive, because the detonation pressure is directly proportional to the squared density ρ^2. In contrast, the detonation velocity depends on the molar quantity N of formed gaseous products and also on the density. Also highly, endothermic heats of formations ($\Delta_f H°$) are required for effective energetic materials.[3] Moreover the new explosive should be cheap to synthesize, stable towards temperature, storable for long

periods, and of course safe to handle. For safety reasons it only should detonate under specific conditions. Increasing environmental concerns over the last few years also raised the requirements of HEDMs, and new replacements for the commonly used toxic RDX are desired.[4] Therefore explosives containing high nitrogen contents are in the focus, because of the environmentally benign dinitrogen N_2 molecule as the reaction product, whereas nitrogen oxides (N_xO_y), NH_3, or HCN are not desired.[5] The high, negative enthalpy of formation for the decomposition products and the diminution of carbon residues are further advantages of nitrogen rich compounds. The following work is about synthesis and characterization of new explosives based on 5-amino-1*H*-tetrazole (**5-AT**) and its derivatives.[6,7] As a result of its considerable nitrogen content and its stability towards impact, friction, and heat and also its cheap availability, it is an appropriate precursor for the formation of new explosives. The stability of **5-AT** is based on the aromatic ring system within the molecular structure of this compound. Substituted

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(1) (a) Klapötke, T. M. In *Moderne Anorganische Chemie*, 3rd ed.; Riedel, E., Ed.; Walter de Gruyter: Berlin, **2007**; pp 99−104. (b) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. *Angew. Chem., Int. Ed.* **2006**, *45* (22), 3584. (c) Chapman, R. D. In *High Energy Density Materials*; Klapötke, T. M., Ed.; Springer: Berlin, **2007**; pp 123−152.
(2) Klapötke, T. M. In *High Energy Density Materials*; Klapötke, T. M., Ed.; Springer: Berlin, **2007**; 85−122.
(3) Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Angew. Chem.* **2000**, *112*, 1861; *Angew. Chem., Int. Ed.* **2000**, *39*, 1791.

(4) Hurley, M.; Klapötke, T. M. Presented at SERDP, Technical Symposium & Workshop, December 4−6, **2007**, Washington, DC.
(5) (a) Hammerl, A.; Hiskey, M. A.; Holl, G.; Klapötke, T. M.; Polborn, K.; Stierstorfer, J.; Weigand, J. J. *Chem. Mater.* **2005**, *17*, 3784–3793. (b) Hammerl, A.; Holl, G.; Klapötke, T. M.; Meyer, P.; Nöth, H.; Piotrowski, H.; Warchhold, M. *Eur. J. Inorg. Chem.* **2004**, *4*, 834–845. (c) Hammerl, A.; Klapötke, T. M.; Nöth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 3570–3575. (d) Klapötke, T. M.; Mayer, P.; Schulz, A.; Weigand, J. J. *J. Am. Chem. Soc.* **2005**, *127*, 2032–2033.
(6) (a) Thiele, J.; Marais, J. T. *J. Liebigs Ann.* **1893**, *273*, 144–160. (b) Thiele, J. *J. Liebigs Ann.* **1898**, *303*, 57–75.
(7) Ernst, V.; Klapötke, T. M.; Stierstorfer, J. *Z. Anorg. Allg. Chem.* **2007**, *633*, 879–887.
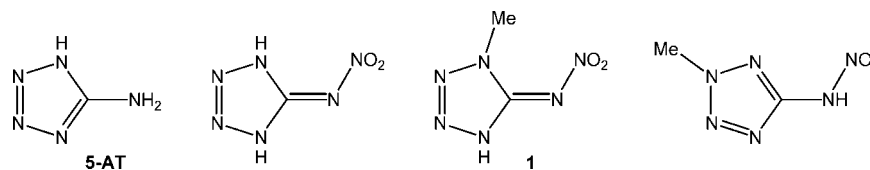
Figure 1. 5-Aminotetrazole (5-AT), 5-nitriminotetrazole, 1-methyl-5-nitriminotetrazole (**1**), and 2-methyl-5-nitriminotetrazole.

derivatives of **5-AT** were extensively investigated in 1950 by Herbst et al.[8] The influence of different substitution groups changes the characteristics of the compound significantly. Alkyl groups substituted at the atoms N1, N2, or C5 raise the stability of the compounds. In contrast, substituted groups with electron acceptor effect destabilize the synthesized compound. To prepare new energetic materials, often tetrazoles,[9] tetrazolates,[10] and tetrazolium[11,12] salts are used since they are mostly endothermic compounds with a high nitrogen content. In addition these compounds are considered mostly less toxic, easy to handle due to their high kinetic and thermal stability, and easy to prepare. A disadvantage of tetrazolates and tetrazolium compounds is the possible contamination of ground water since these ionic structures feature a high solubility. On the other side, they show mostly high densities and stabilities based on their lattice energy. The formation of ionic structures is a popular approach for the synthesis of new energetic materials. It is hard to fulfill all requirements for new energetic materials. However, the compounds described in this work are N-rich salts of the anion 1-methyl-5-nitriminotetrazolate. This is a valuable compound, due to the combination of the nitrogen-rich backbone as a fuel and the nitro group as an oxidizer. The first investigations on neutral 1-methyl-5-nitriminotetrazole (**1**) were published in 1957.[13] In the past, the nomenclature 1-methyl-5-nitraminotetrazole was used since the detailed structure of the molecule had not been discovered. Since we recently published a full characterization of 5-nitriminotetrazoles[14] including the crystals structures, now the nomenclature 5-nitriminotetrazole seems to be correct due to the bond length between the tetrazole ring and the nitramine group. The nitration of the amino group in **5-AT** leads to an increased energetic character as well as higher sensitivities compared to **5-AT** and improves the oxygen balance. The methyl group lowers the sensitivity in comparison to nonmethylated 5-nitriminotetrazole. Deprotonation of 1-methyl-5-nitriminotetrazole yields more suitable compounds with higher decomposition temperatures. For this reason 5-nitriminotetrazolate anions are convenient components for new ionic energetic materials (Figure 1).

According to the performance in energetic salts the same requirements have to be applied for the cations of the energetic material. Therefore 5-nitriminotetrazolate salts containing nitrogen rich cations are the focus of this study. We recently synthesized the ammonium 1-methyl-5-nitriminotetrazolate and ammonium 2-methyl-5-nitriminotetratolate salts, where the second is characterized by a too low decomposition temperature.[15] The ammonium ion is very popular as a result of its environmental compatibility and its structure containing only nitrogen and hydrogen atoms. 1-Methyl-5-nitriminotetrazole as its ammonia salt does not show a resounding thermal stability, but a good kinetic stability, a high density, and acceptable performance. A promising strategy for improving the performance is the replacement of the ammonium ion by cations with higher nitrogen contents. Following this approach different guanidinium salts of **1** were synthesized and are presented in this work. Guanidine chemistry has extended over a period of more than 100 years, and many useful compounds have been identified. The spectrum of uses of these compounds is highly diverse, ranging from biologically active molecules to highly energetic materials, thus indicating the manifold usability of the guanidine moiety as building block.[16]

Experimental Section

Caution! 1-Methyl-5-nitriminotetrazole and its salts are energetic materials with increased sensitivities toward shock and friction. Therefore, proper security precautions (safety glass, face shield, earthened equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds. Specifically, compounds described containing the azido or perchlorate group are extremely sensitive and have to be handled very carefully.

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded using a JEOL Eclipse 270, JEOL EX 400, or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards, such as trimethylsilane (TMS; ^{1}H, ^{13}C) or nitromethane (^{14}N, ^{15}N). To determine the melting points of the described compounds a Linseis PT 10 DSC (heating rate: 5 °C/min) was used. Raman spectra were recorded with a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument, which uses an

(8) Herbst, R. M.; Roberts, C. W.; Harvill, E. J. *J. Org. Chem.* **1951**, *16*, 139–149.
(9) Klapötke, T. M.; Meyer, P.; Schulz, A.; Weigand, J. J. *Propellants, Explos., Pyrotech.* **2004**, *29* (6), 325–332.
(10) Ye, C.; Xiao, J.-C.; Twamley, B.; Shreeve, J. M. *Chem. Commun.* **2005**, *21*, 2750–2752.
(11) Galvez-Ruiz, J. C.; Holl, G.; Karaghiosoff, K.; Klapötke, T. M.; Löhnwitz, K.; Mayer, P.; Nöth, H.; Polborn, K.; Rohbogner, C. J.; Suter, M.; Weigand, J. J. *Inorg. Chem.* **2005**, *44* (14), 4237–4253.
(12) Xue, H.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43* (25), 7972–7977.
(13) Garrison, J. A.; Herbst, R. M. *J. Org. Chem.* **1957**, *22*, 278–83.
(14) Klapötke, T. M.; Stierstorfer, J. *Helv. Chim. Acta* **2007**, *70*, 2137–2160.

(15) Klapötke, T. M.; Laub, H A.; Stierstorfer, J. *Propellants, Explos., Pyrotech.* **2008**, in press.
(16) (a) Fukumoto, S.; Imamiya, E.; Kusumoto, K.; Fujiwara, S.; Watenabe, T.; Shiraishi, M. *J. Med. Chem.* **2002**, *45* (14), 3009–3021. (b) Jedidi, I.; Therond, P.; Zarev, S.; Cosson, C.; Couturier, M.; Massot, C.; Jore, D.; Gardes-Albert, M.; Legrand, A.; Bonnefondt-Rousselot, D. *Biochemistry* **2003**, *42* (38), 11356–11365. (c) Schug, K. A.; Lindner, W. *Chem. Rev.* **2005**, *105* (1), 67–114. (d) Nineham, A. W. *Chem. Rev.* **1955**, *55* (2), 355–483. (e) Brothrton, T. K.; Lynn, J. W. *Chem. Rev.* **1959**, *59* (5), 841–883. (f) Neutz, J.; Grosshardt, O.; Schäufele, S.; Schnupper, H.; Schweikert, W. *Propellants, Explos., Pyrotech.* **2003**, *28* (4), 181–188. (g) Wingborg, N.; Latypov, N. *Propellants, Explos., Pyrotech.* **2003**, *28* (6), 314–318.

Nd:YAG laser with a wavelength of 1064 nm. Infrared (IR) spectra were recorded using a Perkin-Elmer One FT-IR instrument with ATR unit. Bomb calorimetry was performed with a Parr 1356 Bomb calorimeter employing a Parr 207A oxygen bomb. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer was employed.

1-Methyl-5-nitriminotetrazole (**1**) was prepared according to the literature.[14] Also potassium 1-methyl-5-nitriminotetrazolate was obtained by the recently published procedure.[27] Guanidinium chloride and diaminoguanidinium chloride are commercially available. Aminoguanidinium chloride was synsized by neutralization of commercially available aminoguanidine bicarbonate with 2 N HCl followed by recrystallization from water/ethanol. Triaminoguanidinium chloride is obtained by the reaction of AG_Cl with an excess of hydrazine hydrate in dioxane and recrystallization from water/ethanol. Azidoformamidinium chloride was prepared by the reaction of AG_Cl with 1 equiv of NaNO$_2$ and HCl, followed by a recrystallization from water/ethanol. Guanidinium perchlorates were synthesized according to literature.[17]

Silver 1-Methyl-5-nitriminotetrazolate (3). Silver nitrate (1.70 g, 0.01 mol) was dissolved in 20 mL of water and added to a solution of potassium 1-methyl-5-nitriminotetrazolate (**2**) (1.82 g, 0.01 mol) in 20 mL of water. The silver salt precipitated immediately as a colorless powder. The reaction mixture was stirred for 30 min under exclusion of light. The product was filtered off and dried using high vacuum also under the exclusion of light. To obtain suitable crystals for X-ray diffraction analysis small amounts of product **3** were recrystallized from hot water. (2.42 g, yield; 97 %). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2966 (w), 1505 (s), 1456 (s), 1400 (m), 1381 (m) 1329 (vs), 1301 (vs), 1260 (m), 1232 (s), 1123 (m), 1052 (w), 1034 (w), 985 (w), 878 (w), 764 (w), 756 (w), 728 (w), 696 (w). Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2986 (35), 2971 (14), 1503 (100), 1463 (19), 1403 (14), 1387 (13), 1331 (20), 1306 (25), 1233 (11), 1124 (14), 1034 (66), 987 (5), 880 (8), 758 (23), 730 (5), 688 (14), 504 (20), 466 (5), 372 (8), 303 (19), 245 (7), 211 (8), 86 (4). Elem anal. (C$_2$H$_3$N$_6$AgO$_2$, M250.95) Calcd: C, 9.57; H, 1.20; N, 33.49 %. Found: C, 10.10; H, 1.51; N, 33.08 %. BAM-Drophammer, >50 J; BAM-Friction Test, >360 N.

Guanidinium 1-Methyl-5-nitriminotetrazolate (4). Potassium 1-methyl-5-nitriminotetrazolate (3.34 g, 0.02 mol) was dissolved in 20 mL of water. Under constant stirring a solution of silver nitrate (3.38 g, 0.02 mol) in water was added. **3**, which started instantly to precipitate, was filtered and washed with small amounts of water. The wet powder was completely transferred into a reaction vessel, which contained a solution of guanidinium chloride (1.62 g, 0.02 mol) in water. Silver chloride started to precipitate immediately, indicating the successful course of the reaction. The silver chloride was filtered off, and the filtrate was collected in a volumetric reaction flask. The solvent was removed by a rotary evaporator. To purify product **4** the solid residue was recrystallized from an EtOH/H$_2$O (4:1) mixture. Analytically pure **4** was achieved as colorless needles after filtration and washing with EtOH and diethyl ether. (3.17 g, yield 78 %) could be obtained. All steps should be performed under exclusion of light. Mp 192 °C, 210 °C (dec.) (DSC, 5°/min). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3433 (s), 3350 (s), 3282 (s), 3173 (vs), 2955 (m), 2796 (w), 1666 (s), 1654 (s), 1595 (w), 1556 (w), 1505 (m), 1455 (m), 1412 (w), 1323 (vs), 1234 (s), 1123 (s), 1039 (m), 1006 (m), 888 (m), 767 (w), 748 (w), 737 (m), 686 (m). Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2987 (9), 2959 (9), 1514 (100), 1459 (24), 1325 (17), 1298 (27), 1236 (8), 1127 (22), 1042 (81), 1009 (23), 890 (8), 750 (13), 688 (16), 544 (7), 499 (8), 370

(8), 296 (19). ^{1}H NMR (DMSO-d_6, 25 °C) δ = 6.94 (s, 6H, NH$_2$), 3.68 (s, 3H, CH$_3$). ^{13}C NMR (DMSO-d_6, 25 °C) δ = 158.4 (G$^+$), 157.6 (CN$_4$), 33.1 (CH$_3$). m/z (FAB$^+$): 60 (cation). m/z (FAB$^-$): 143 (anion). Elem anal. (C$_3$H$_9$N$_9$O$_2$, M = 203.16) Calcd: C, 17.74; H, 4.47; N, 62.05 %. Found: C, 17.69; H, 4.35; N, 61.76 %. BAM-Drophammer, >40 J; BAM-Friction Test, >360 N. ΔU_{comb}: 12.95 kJ g^{-1}.

Aminoguanidinium 1-Methyl-5-nitriminotetrazolate (5). The synthesis of **5** proceeded analogously to the synthesis of **4**. Potassium 1-methyl-5-nitriminotetrazolate (3.34 g, 0.02 mol) and aminoguanidinium chloride (2.21 g, 0.02 mol) were used as starting materials. After recrystallization from water/ethanol colorless crystals were obtained. (3.75 g, yield 86 %) Mp 154 °C, 216 °C (dec.) (DSC, 5°/min). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3430 (m), 3354 (s), 3252 (s), 3142 (s), 1657 (vs), 1505 (m), 1459 (s), 1342 (vs), 1322 (vs), 1294 (vs), 1234 (s), 1217 (s), 1102 (m), 1031 (m), 949 (m), 880 (m), 772 (w), 738 (w), 690 (m). Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3285 (4), 2986 (27), 2959 (9), 1670 (6), 1508 (100), 1461 (34), 1415 (11), 1390 (5), 1323 (31), 1307 (21), 1239 (4), 1116 (15), 1034 (99), 969 (14), 885 (11), 747 (19), 694 (16), 621 (4), 507 (21), 457 (6), 372 (6), 296 (34), 201 (10). ^{1}H NMR (DMSO-d_6, 25 °C) δ = 8.57 (s, 1H, NH−NH$_2$), 7.24 (s, 2H, NH$_2$), 6.75 (s, 2H, NH$_2$), 4.68 (s, 2H, NH−NH$_2$), 3.66 (s, 3H, CH$_3$). ^{13}C NMR (DMSO-d_6, 25 °C) δ = 159.3 (AG$^+$), 157.7 (CN$_4$), 33.1 (CH$_3$). m/z (FAB$^+$): 75 (cation). m/z (FAB$^-$): 143 (anion). Elem anal. (C$_3$H$_{10}$N$_{10}$O$_2$, M = 218.18) Calcd: C, 16.52; H, 4.62; N, 64.20 %. Found: C, 16.51; H, 4.75; N, 63.79 %. BAM-Drophammer, >10 J. BAM-Friction Test: >360 N. ΔU_{comb}: 13.18 kJ g^{-1}.

Diaminoguanidinium 1-Methyl-5-nitriminotetrazolate (6). The synthesis of **6** proceeded analogously to the synthesis of **4**. Potassium 1-methyl-5-nitriminotetrazolate (3.34 g, 0.02 mol) and diaminoguanidinium chloride (2.51 g, 0.02 mol) were used as starting materials. After recrystallization from water/ethanol, colorless crystals were obtained. (3.82 g, yield 82 %) Mp 120 °C, 208 °C (dec.) (DSC, 5°/min). IR (KBr, cm^{-1}): $\tilde{\nu}$ =3468 (m), 3364 (w), 3311(s), 3246 (s), 3203 (s), 1672 (m), 1617 (w), 1506 (s), 1456 (s), 1407 (m), 1341 (vs), 1294 (vs), 1228 (s), 1162 (m), 1108 (s), 1036 (s), 947 (m), 880 (m), 772 (w), 740 (m), 686 (m). Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3354 (17), 2986 (15), 2959 (8), 1518 (100), 1464 (25), 1297 (41), 1178 (8), 1111 (13), 1039 (99), 927 (13), 889 (11), 755 (21), 691 (18), 551 (9), 494 (11), 369 (13), 292 (17), 192 (12). ^{1}H NMR (DMSO-d_6, 25 °C) δ = 8.54 (s, 2H, NH−NH$_2$), 7.16 (s, 2H, C=NH$_2$), 4.59 (s, 4H, NH−NH$_2$), 3.67 (s, 3H, CH$_3$). ^{13}C NMR (DMSO-d_6, 25 °C) δ = 160.3 (DAG$^+$), 157.7 (CN$_4$), 33.1 (CH$_3$). m/z (FAB$^+$): 90 (cation). m/z (FAB$^-$): 143 (anion). Elem anal. (C$_3$H$_{11}$N$_{11}$O$_2$, M = 233.19) Calcd: C, 15.45; H, 4.75; N, 66.07 %. Found: C, 15.32; H, 4.88; N, 65.71 %. BAM-Drophammer, >7.5 J; BAM-Friction Test, >360 N. ΔU_{comb}: 13.36 kJ g^{-1}.

Triaminoguanidinium 1-Methyl-5-nitriminotetrazolate (7). The synthesis of **7** proceeded analogously to the synthesis of **4**. Potassium 1-methyl-5-nitriminotetrazolate (3.34 g, 0.02 mol) and triaminoguanidinium chloride (2.80 g, 0.02 mol) were used as starting materials. After recrystallization from water/ethanol, colorless needles were obtained. (4.52 g, yield 91 %) Mp 158 °C, 210 °C (dec.) (DSC, 5°/min). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3469 (w), 3371 (m), 3322 (vs), 3207 (s), 1676 (s), 1618 (w), 1507 (s), 1455 (vs), 1340 (vs), 1228 (s), 1194 (m), 1132 (m), 1107 (s), 1036 (m), 979 (m), 880 (m), 773 (m), 739 (m), 687 (m). Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3331 (20), 3229 (12), 2986 (16), 1506 (100), 1462 (32), 1418 (17), 1295 (35), 1228 (11), 1108 (20), 1038 (94), 978 (12), 894 (21), 754 (18), 691 (23), 637 (10), 489 (17), 414 (13), 301 (21), 207 (18). ^{1}H NMR (DMSO-d_6, 25 °C) δ = 8.60 (s, 3H, NH−NH$_2$), 4.50 (s, 6H, NH−NH$_2$), 3.67 (s, 3H, CH$_3$).

(17) Klapötke, T. M.; Stierstorfer, J. *Cent. Eur. J. Energ. Mat.* **2008**, *5* (1), 13–30.

**Scheme 1. Syntheses of Compounds 4−8 via the Formation of AgCl**

Cat⁺ =   G⁺   AG⁺   DAG⁺   TAG⁺   AF⁺
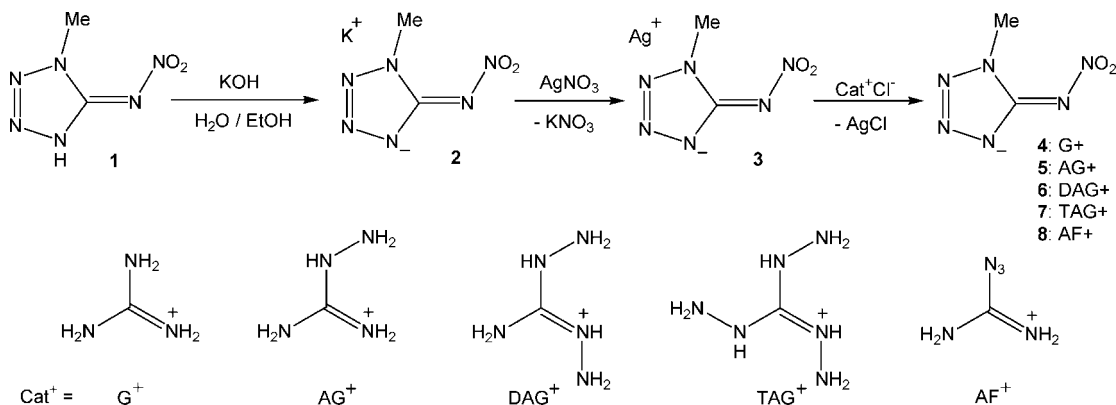
^{13}C NMR (DMSO-d_6, 25 °C) δ = 159.6 (Tag$^+$), 157.7 (CN$_4$), 33.1 (CH$_3$). ^{15}N NMR (DMSO-d_6, 25 °C) δ = 4.45 (N3), −14.12 (N6), −18.29 (N2, t, $^3J_{NH}$ = 1.9 Hz), −71.15 (N4), −157.16 (N5), −168.38 (N1, d, $^2J_{NH}$ = 2.2 Hz), −289.13 (N7, $^1J_{NH}$ = 102.7 Hz), −329.66 (N8, $^1J_{NH}$ = 69.4 Hz). m/z (FAB$^+$): 105 (cation). m/z (FAB$^-$): 143 (anion). Elem anal. (C$_3$H$_{12}$N$_{12}$O$_2$, M = 248.21) Calcd: C, 14.52; H, 4.87; N, 67.72 %. Found: C, 14.52; H, 4.77; N, 67.45 %; BAM-Drophammer, >6 J; BAM-Friction Test, >240 N. $\Delta U_{comb.}$: 14.01 kJ g^{-1}.

Azidoformamidinium 1-Methyl-5-nitriminotetrazolate (8). The synthesis of **8** proceeded analogously to the synthesis of **4**. Potassium 1-methyl-5-nitriminotetrazolate (3.34 g, 0.02 mol) and azidoformamidinium chloride (2.80 g, 0.02 mol) were used as starting materials. After recrystallization from water/ethanol colorless needles were obtained (2.43 g, yield 91 %). Since **8** is well soluble in EtOH, the white, solid residuum could not be recrystallized from an EtOH/water mixture. Therefore it was filtered off and the colorless, microcrystalline powder was washed three times with small amounts of cold acetone. Residues of acetone were removed by high-vacuum. (4.25 g, yield 93 %) Mp 118 °C, 165 °C (dec.) (DSC, 5°/min). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3396 (m), 3325 (m), 3235 (s), 3186 (s), 2963 (m), 2796 (m), 2440 (w), 2354 (w), 2187 (s), 2112 (w), 1699 (s), 1660 (s), 1571 (w), 1507 (s), 1462 (s), 1407 (m), 1380 (m), 1312 (vs), 1295 (vs), 1240 (s), 1227 (vs), 1124 (m), 1106 (s), 1051 (m), 1032 (s), 981 (m), 902 (m), 884 (m), 772 (m), 732 (m), 690 (s), 659 (m), 580 (m). Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2986 (21), 2958 (8), 2189 (18), 2112 (3), 1659 (2), 1521 (91), 1469 (52), 1411 (5), 1360 (20), 1302 (44), 1239 (5), 1120 (33), 1059 (5), 1042 (100), 990 (4), 900 (18), 760 (19), 703 (10), 693 (15), 658 (10), 504 (10), 486 (12), 464 (8), 368 (12), 290 (11), 233 (12), 196 (16), 159 (10). ^{1}H NMR (DMSO-d_6, 25 °C) δ = 9.10 (s, 2H, NH_2), 8.72 (s, 2H, NH_2), 3.75 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 25 °C) δ = 159.2 (AF$^+$), 157.1 (CN$_4$), 33.8 (CH$_3$). ^{15}N NMR (D$_2$O, 25 °C) δ = −12.35 (N3), −19.03 (N6), −24.68 (N2, q, $^3J_{NH}$ = 1.9 Hz), −97.11 (N4), −138.97 (N8), −152.72 (N9), −158.46 (N5), −171.48 (N1, q, $^2J_{NH}$ = 2.2 Hz), −277.64 (N7), −291.81 (N10). m/z (FAB$^+$): 86 (cation). m/z (FAB$^-$): 143 (anion). Elem anal. (C$_3$H$_7$N$_{11}$O$_2$, M = 229.16) Calcd: C, 15.72; H, 3.08; N, 67.23 %. Found: C, 15.31; H, 3.09, N, 65.68 %; BAM-Drophammer, >4 J; BAM-Friction Test, >160 N. $\Delta U_{comb.}$: 11.34 kJ g^{-1}.

Aminoguanidinium 1-Methyl-5-nitriminotetrazolate (5). 1-Methyl-5-nitriminotetrazole (7.20 g, 50 mmol) dissolved in 50 mL of water was reacted with a suspension of aminoguanidine bicarbonate (6.8 g, 50 mmol). The solution was stirred for 5 min at 50 °C. Subsequently the solvent was removed under vacuum. The analytically pure product (**5**) was washed with 50 mL of an ethanol/diethyl ether mixture and separated by filtration (10.6 g, 97 % yield).

Scheme 2. Syntheses of Compounds 4−8 via the Formation of KClO$_4$
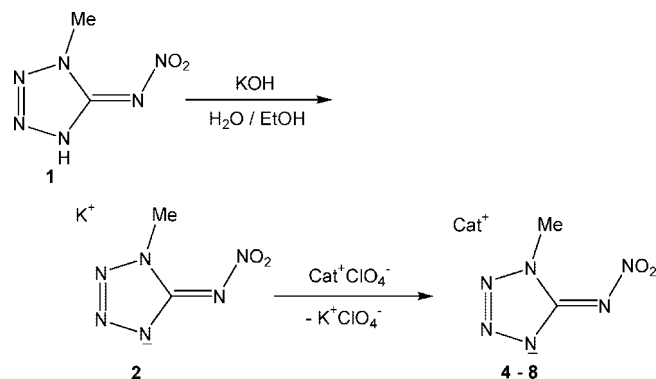
Triaminoguanidinium 1-Methyl-5-nitriminotetrazolate (7). To **5** (8.73 g, 40 mmol) were added 50 mL of dioxane, 10 mL of water, and hydrazine hydrate (4.10 g, 82 mmol). The mixture was heated to 90 °C for 3 h. Afterwards the solvent was evaporated and precipitation was initiated by the addition of small amounts of ethanol and diethyl ether. The crude product was recrystallized from a hot ethanol/water (10:1) mixture (8.2 g, 83 % yield).

Results and Discussion

Synthesis. Scheme 1 shows a general survey of syntheses of the guanidinium 1-methyl-5-nitriminotetrazolate salts. All these compounds were synthesized using silver 1-methyl-5-nitriminotetrazolate (**3**), which was used in the wet state. **3** was obtained by metathesis reaction of potassium 1-methyl-5-nitriminotetrazolate (**2**) and silver nitrate. The reaction products guanidinium 1-methyl-5-nitriminotetrazolate (**4**), 1-aminoguanidinium 1-methyl-5-nitriminotetrazolate (**5**), 1,3-diaminoguanidinium 1-methyl-5-nitriminotetrazolate (**6**), 1,3,5-triaminoguanidinium 1-methyl-5-nitriminotetrazolate (**7**), and azidoformamidinium 1-methyl-5-nitriminotetrazolate (**8**) were formed by the reaction of **3** with the correspondent chloride salts. Thereby the impetus of these reactions is the formation of silver chloride, which features a very low solubility in water and can be easily removed by filtration.

An alternative procedure to yield **4−8** is the reaction of the potassium salt **2** and the corresponding guanidinium perchlorates under the formation of low soluble potassium perchlorate. This method does not include an intermediate, and therefore the reaction yields are slightly better and nearly quantitative. As the perchlorates are more sensitive than the chlorides, appropriate security measures have to be applied.

Table 1. X-ray Data and Parameters

	3	**4**	**6**	**7**	**8**
formula	$C_2H_3AgN_6O_2$	$C_3H_9N_9O_2$	$C_3H_{13}N_{11}O_3$	$C_3H_{12}N_{12}O_2$	$C_3H_7N_{11}O_2$
formula weight [g mol^{-1}]	250.97	203.19	251.24	248.25	229.20
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
color/habit	colorless blocks	colorless needles	colorless needles	colorless needles	colorless needles
size [mm]	$0.03 \times 0.08 \times 0.09$	$0.05 \times 0.17 \times 0.22$	$0.04 \times 0.13 \times 0.19$	$0.09 \times 0.13 \times 0.14$	$0.09 \times 0.12 \times 0.14$
a [Å]	10.7740(3)	21.2356(8)	7.081(2)	6.8650(2)	7.9410(2)
b [Å]	8.4315(2)	6.8969(2)	7.361(2)	7.9800(2)	6.7131(1)
c [Å]	6.4111(2)	12.1761(4)	10.515(3)	10.5180(3)	17.7867(3)
α [deg]	90.0	90.0	80.68(2)	101.311(2)	90.0
β [deg]	103.816(3)	102.457(2)	88.59(2)	103.776(2)	95.269(2)
γ [deg]	90.0	90.0	74.05(2)	103.123(2)	90.0
V [Å^3]	565.54(3)	574.1(1)	519.9(3)	525.60(3)	944.18(3)
Z	4	8	2	2	4
ρ_{calcd} [g cm^{-3}]	2.948	1.550	1.605	1.569	1.612
μ [mm^{-1}]	3.513	0.129	0.137	0.130	0.135
$F(000)$	480	848	264	260	472
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100	200	100	200	100
θ min, max [deg]	3.9, 26.2	3.5, 25.3	3.8, 26.3	3.2, 26.0	3.8, 26.0
dataset	−13:13; −10:10; −7:7	−25:25; −7:8; −14:14	−8:8; −9:9; −13:13	−8:8; −9:9; −12:12	−9:9; −8:8; −21:21
reflections collected	5491	5055	5496	3943	9050
independent reflections	1130	1574	2086	2056	1855
R_{int}	0.025	0.034	0.021	0.011	0.026
observed reflections	970	1330	1669	1886	1580
parameters	112	164	206	202	173
R_1 (obs)	0.0190	0.0487	0.0315	0.0354	0.0298
wR_2 (all data)	0.0494	0.1359	0.0889	0.1131	0.0735
GOF	1.08	1.15	1.11	1.19	1.08
resd. dens. [e/Å^3]	−0.58, 1.48	−0.26, 0.26	−0.26, 0.20	−0.43, 0.30	−0.24, 0.19
device type	Oxford Xcalibur3 CCD	Kappa CCD	Oxford Xcalibur3 CCD	Kappa CCD	Oxford Xcalibur3 CCD
solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
refinement	SHELXL−97	SHELXL−97	SHELXL−97	SHELXL−97	SHELXL−97
absorption correction	multi-scan	none	multi-scan	none	multi-scan
CCDC	670917	670921	670918	670920	670919

A further facile route to **4** and **5** is the reaction of **1** with commercially available bis(guanidinium) carbonate and aminoguanidine bicarbonate.

Molecular Structures. To determine the molecular structures of **3**, **6**, and **8** in the crystalline state an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector was used. The data collection was performed using the CrysAlis CCD software,[18] and the data reductions were performed with the CrysAlis RED software.[19] The solutions of all structures were performed using SIR-92,[20] SHELXS-97,[21] and SHELXL-97[22] implemented in the WinGX software package[23] and finally checked with the PLATON software.[24] In all crystal structures the hydrogen atoms were located and refined. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method.[25]

The X-ray work on **4** and **7** was done on a Nonius Kappa CCD diffractometer, whereas the data collection and reduction was done by the Bruker "Collect" as well as the "HKL Denzo and Scalepack" software.

Selected data and parameters of the X-ray determinations are given in Table 1. Further information on the crystal-structure determinations is in Supporting Information and has been deposited with the Cambridge Crystallographic Data Centre[26] as supplementary publication Nos. 670917 (**3**), 670918 (**4**), 670919 (**6**), 670920 (**7**), and 670921 (**8**).

1-Methyl-5-nitriminotetrazole and its crystal structure were recently investigated and published by our research group.[14] Its structure is very similar compared to the molecular structures of the anions in the investigated 1-methyl-5-nitriminotetrazolate salts. Only the position of the nitramine group to the tetrazole ring plane differs significantly since there are various hydrogen bonds influencing this building block. Geometric details (lengths, angles, and torsion angles) of all crystal structures can be found in the Supporting Information.

The silver salt **3** crystallizes in the monoclinic space group $P2_1/c$, with four formula units in the unit cell resulting in a calculated density of 2.947 g cm^{-3}. Figure 2 represents the asymmetric unit and its labeling scheme. The distances between the tetrazole ring atoms conform to the results for **4**, **6**, **7**, and **8** and are described in detail in the structure of **4**. The tetrazole ring is planar (torsion angle N1−C1−N4−N3

(18) *CrysAlis CCD*, Version 1.171.27p5 beta; Oxford Diffraction Ltd.
(19) *CrysAlis RED*, Version 1.171.27p5 beta; Oxford Diffraction Ltd.
(20) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(21) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, **1997**.
(22) Sheldrick, G. M. *Shelxl-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1994**.
(23) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
(24) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht, The Netherlands, 1999.
(25) *SCALE3 ABSPACK-An Oxford Diffraction program*; Oxford Diffraction Ltd., **2005**.

(26) Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code_(1223)336-033. E-mail for inquiry: fileserv@ccdc.cam.ac.uk. E-mail for deposition: deposit-@ccdc.cam.ac.uk).
(27) Klapötke, T. M.; Radies, H.; Stierstorfer, J. *Z. Naturforsch.* **2007**, *62b*, 1343–1352.
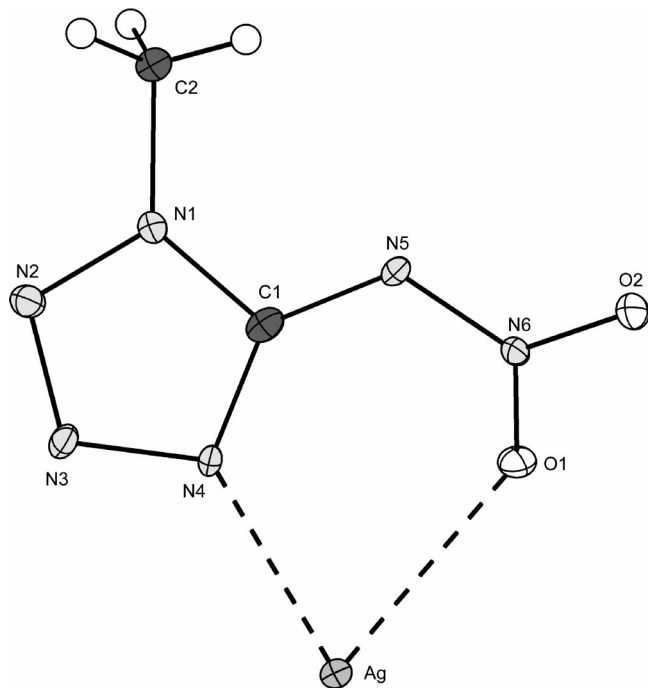
Figure 2. Formula unit of silver 1-methyl-5-nitriminotetrazolate (**3**). Thermal ellipsoids represent the 50% probability level.
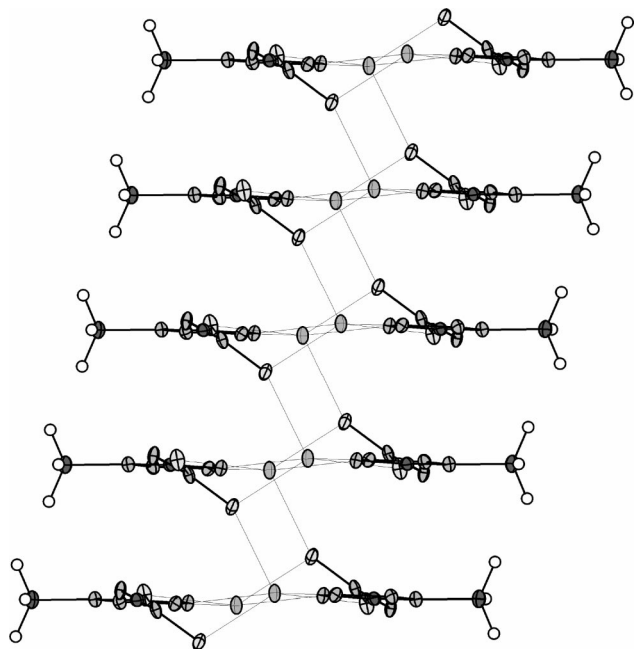

Figure 3. View on the 2-dim layers in the crystal structure of **3** along axis *b*.

= −0.9(3)°), indicating a delocalized, aromatic π system. The nitramine group is considerably twisted out of this plane (torsion angle N4−C1−N5−N6 = 31.8(5)°), and the bond length C1−N5 (1.37(4) Å) corresponds more to a C=N double bond. This result is very similar to latest investigations on alkali salts of 1-methyl-5-nitriminotetrazole.[27]

The ions of compound **3** are packed in a complex three-dimensional structure, which contains endless, two-dimensional layers as structural units, which are illustrated in Figure 3. As no classic hydrogen bonds can be detected in the crystal, the packing is only influenced by electrostatic forces. Within this structure the silver cations are pentacoordinated
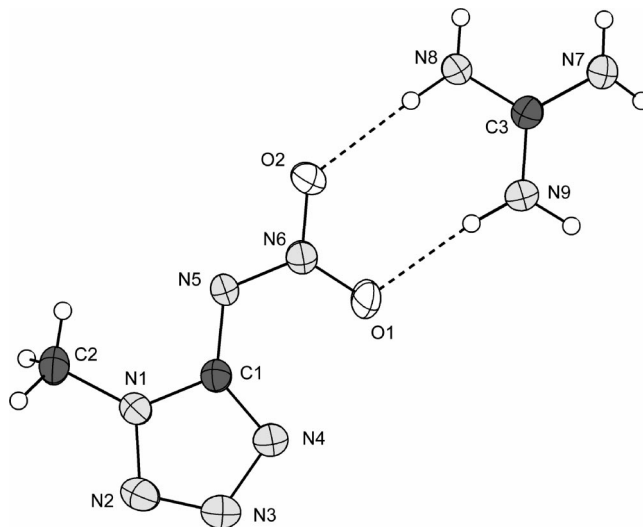
Figure 4. Formula unit of **4**. Thermal ellipsoids represent the 50% probability level.

by the *N*,*O*-chelating nitriminotetrazolate with d(Ag1−N4) = 2.27(2) Å and d(Ag1−O1) = 2.61(3) Å, by the oxygen atom of a neighboring tetrazolate d(Ag1−O1^i) = 2.77(4) Å [(i) x, −0.5 − y, 0.5 + z], by one nitrogen atom with d(Ag1−N3^{ii}) = 2.33 Å [(ii) 1 − x, −0.5 + y, 1.5 − z], and by the nitro group of another neighboring 5-nitriminotetrazolate anion with d(Ag1−O2^{iii}) = 2.46(2) Å [(iii) 1 − x, 0.5 + y, 1.5 − z]. The geometry of this coordination can be described as a distorted trigonal bipyramide. The distances for the metal coordinating bonds are very similar compared to those found in alkali 5-nitriminotetrazolates.[27]

Figure 4 shows the molecular moiety of guanidinium 1-methyl-5-nitriminotetrazolate (**4**), which crystallizes in the monoclinic space group *C*2/*c*. There are eight formula moieties in the unit cell, and the crystal structure features a density of 1.550 g cm^{-3}. The C−N distances in the cations vary from 1.30 to 1.32 Å, which is between the typical values for C−N single bonds (1.47 Å) and C=N double bonds (1.22 Å),[28] and show the delocalization of the positive charge. The observed bond lengths in the guanidinium cation match the typical values found in the literature for guanidinium nitrate[29] and guanidinium chloride.[30] The tetrazolate ring is again planar (torsion angle C1−N1−N2−N3 = −0.1(3)°). In contrast to this, the nitramine unit is significantly twisted from the ring plane (torsion angle N4−C1−N5−N6 = 8.2(4)°). The bond lengths between the tetrazolate ring atoms N1, N2, N3, and N4 vary from 1.29 to 1.36 Å and fit exactly in the range between N−N single bonds (1.45 Å) an N=N double bonds (1.25 Å).[31] Also the distances between C1−N1 (1.35(4) Å) and C1−N4 (1.33(3) Å) lie within the values for C−N single and C=N double bonds. In contrast to this, the bond N1−C2 (1.46(3) Å), which links the methyl group to the tetrazolate ring, can definitely be identified as a C−N single bond. As the bond N5−N6 (d = 1.31(2) Å) can be

(28) Wiberg, N. *Lehrbuch der Anorganischen Chemie/Holleman-Wiberg*, 101st ed.; Walter de Gruyter, Berlin, **1995**; p 1842.
(29) Akella, A.; Keszler, D. A. *Acta Crystallogr.* **1994**, *C50*, 1974–1976.
(30) Bryden, J. H. *Acta Crystallogr.* **1957**, *10*, 677–680.
(31) N−N values and N=N values from *International tables for X-ray crystallography*; Kluwer Academic Publisher: Dordrecht, The Netherlands, **1992**; Vol. C.
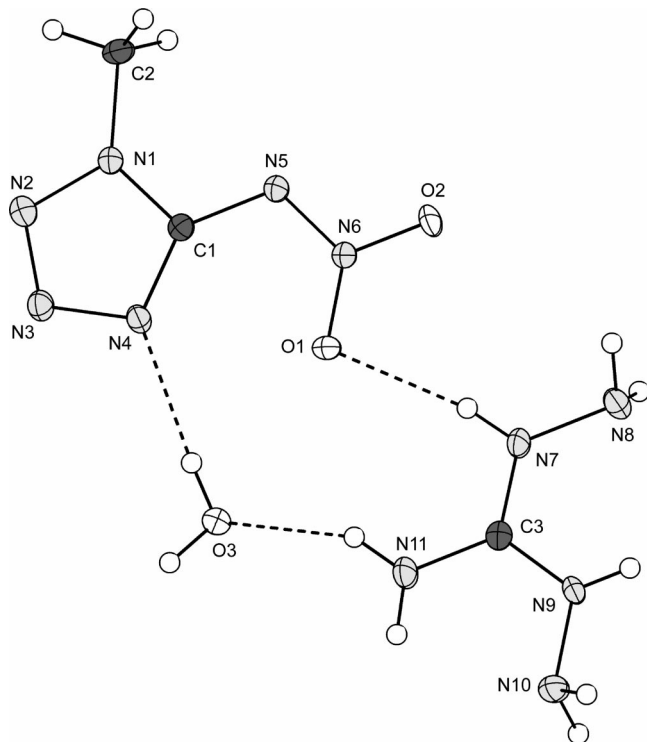
Figure 5. Molecular moiety of **6**. Thermal ellipsoids represent the 50 % probability level.

Figure 6. Molecular moiety of **7**. Thermal ellipsoids represent the 50 % probability level.

identified neither as a single nor as a double bond, also the electrons within the nitramine group participate in the delocalization.

The packing of the crystal structure of **4** is dominated by several classical hydrogen bonds. Thus of these bridges the cations and anions are linked as one-dimensional, infinite chains. This motif is responsible for the package of the crystal. One hydrogen atom, bonded to N7 at the guanidinium cation of one chain, interacts with the atoms N4 and O1 of the 1-methyl-5-nitriminotetrazolate of a second chain, which link the chains to each other.

Although aminoguanidinium 1-methyl-5-nitriminotetrazolate (**5**) could be recrystallized from wet ethanol forming colorless crystals, a suitable solution of the X-ray determination was not practicable due to an unsolvable twin problem. The elemental analysis confirmed no inclusion of crystal water.

Figure 5 shows the molecular moiety of diaminoguanidinium 1-methyl-5-nitriminotetrazolate (**6**) and its labeling scheme. It crystallizes in the triclinic space group $P\bar{1}$, with two formula units in the unit cell and a calculated density of 1.605 g cm^{-3}. The bond lengths within the 1-methyl-5-nitriminotetrazolate fit the values, observed for **4**, almost exactly. In contrast to that the sterical constitution of the nitramine group to the ring plane is different. The aromatic cycle and the nitramine group lie together in one plane (torsion angle N4−C1−N5−N6 = 0.4(2)°). Only the oxygen atoms O1 and O2 are slightly twisted out of the plane (torsion angles C1−N5−N6−O1 = 1.5(2)°, C1−N5−N6−O2 = −178.5(1)°). The distances N7−C3 (d = 1.33(6) Å), N9−C3 (d = 1.32(2) Å), and N11−C3 (d = 1.33(2) Å) within the diaminoguanidinium cation are comparable to the geometry
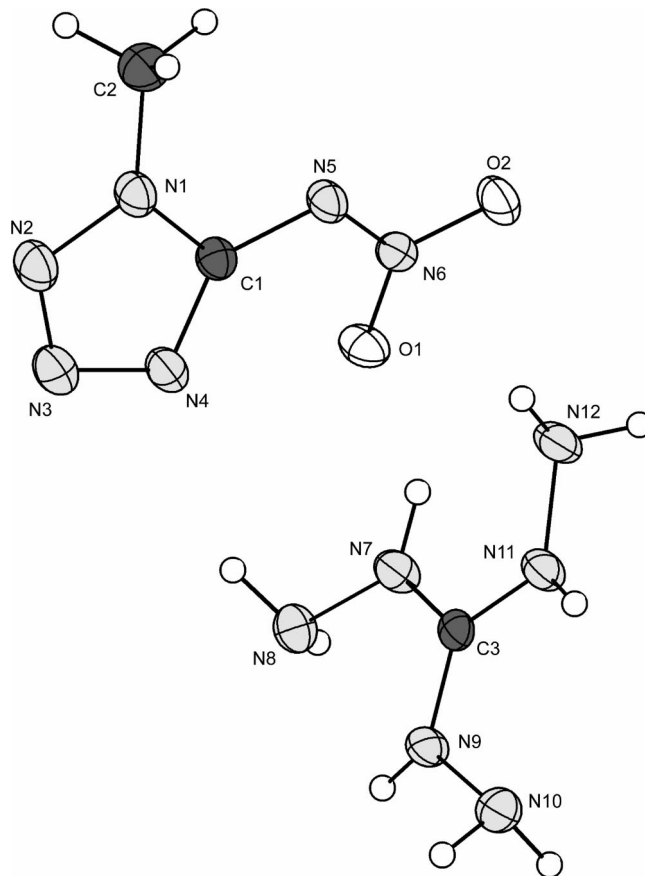
found in diaminoguanidinium 3-nitro-1,2,4-triazol-5-one[32] and are slightly longer than the values found in the guanidinium cation (**4**), which can be explained by the influence of the two additional amino groups. The hydrazine bonds (d(N7−N8) = 1.41(2) Å, d(N9−N10) = 1.41(7) Å) are marginally shorter than the bonds in isolated hydrazine (1.45 Å).[33]

The packing of the structure is again influenced by several classical hydrogen bonds. The ions are packed as two-dimensional, infinite layers within the crystal structure. In these layers one anion is coordinated by three cations and two molecules of crystal water via five hydrogen bonds. These two-dimensional structural units are arranged in a parallel way and connected via hydrogen bonds. The distance between two infinite layers is approximately 5 Å.

The unit cell of triaminoguanidinium 1-methyl-5-nitriminotetrazolate (**7**, Figure 6), which crystallizes with a calculated density of 1.569 g cm^{-3} in the triclinic space group $P\bar{1}$, contains two formula moieties. The bond lengths in the 1-methyl-5-nitriminotetrazolate anion are also very similar to the values found and discussed for **4** and **5**. Although again there are differences in the sterical constitution compared to **6**, which can be seen on the nitramine group strongly twisted out of the aromatic ring plane (torsion angle N4−C1−N5−N6 = 16.9(3)°). Even the oxygen atoms O1 and O2 of the nitro

(32) Cromer, D. T.; Hall, J. H.; Le, K.-Y.; Ryan, R. R. *Acta Crystallogr.* **1988**, *C44*, 2206–2208.
(33) Wiberg, N. *Lehrbuch der Anorganischen Chemie/Holleman-Wiberg*, 101st ed.; Walter de Gruyter, Berlin, **1995**; p 661.
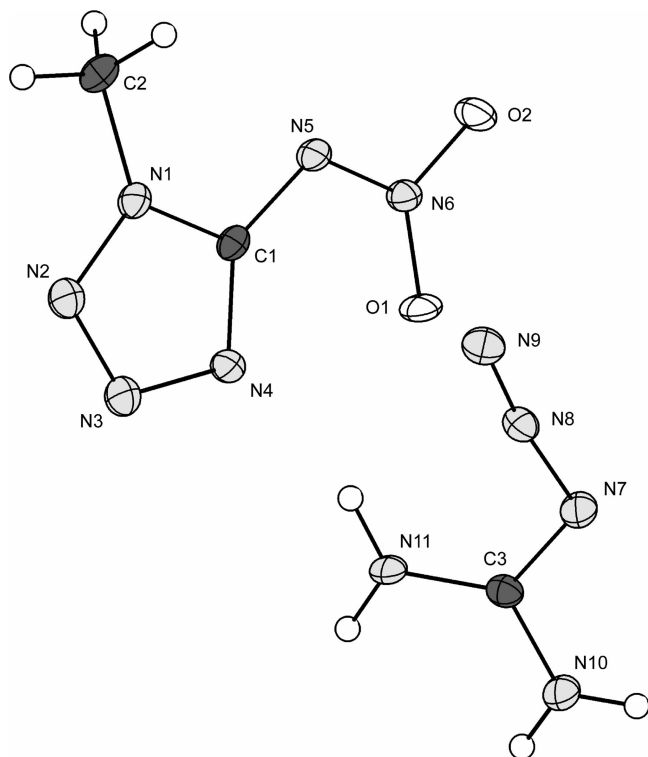
Figure 7. Molecular moiety of **8**. Thermal ellipsoids represent the 50 % probability level.

Figure 8. ^{15}N NMR spectra of **7** and **8**. **7**: δ = 4.5 (N3), −14.1 (N6), −18.3 (N2, q, $^3J_{NH}$ = 1.9 Hz), −71.2 (N4), −157.2 (N5), −168.4 (N1, q, $^2J_{NH}$ = 2.2 Hz), −289.1 (N7, d, $^1J_{NH}$ = 102.7 Hz), −329.7 (N8, t, $^1J_{NH}$ = 69.4 Hz) ppm. **8**: δ = −12.4 (N3), −19.0 (N6), −24.7 (N2, q, $^3J_{NH}$ = 1.9 Hz), −97.1 (N4), −139.0 (N10), −152.7 (N11), −158.5 (N5), −171.5 (N1, q, $^2J_{NH}$ = 2.2 Hz), −277.6 (N12), −291.8 (N9).

group stick significantly up the ring plane (torsion angles N4−C1−N5−O1 = 17.8(2)°, N4−C1−N5−O2 = 15.3(2)°). Within the triaminoguanidinium cation the bond lengths correspond exactly to the values of **6** and those observed for triaminoguanidinium nitrate.[34]

There are several moderate hydrogen bonds which strongly influence the packing of the crystal structure of **8**. Each N−H or N−H$_2$ group of the triaminoguanidinium ion acts as hydrogen bond donor, thus the coordination of this cations dominates the resulting structure. Since the interactions via hydrogen bonds are mostly weak and there are no layers or chains, the packing of **8** is not as dense as those observed for **4** and **6**.

Azidoformamidinium 1-methyl-5-nitrimintetratolate (**8**) crystallizes in the monoclinic space group $P2_1/c$, with four molecules in the unit cell and a calculated density of 1.612 g cm^{-3}. The asymmetric unit and its labeling scheme are displayed in Figure 7. The sterical constitution of the anion in **8** is comparable to that observed for compound **4**. Again the nitramine group is twisted out of the aromatic ring plane (torsion angle N4−C1−N5−N6, 6.9(2)°). The geometry of the azidoformamidinium cation corresponds to that of azidoformamidinium chloride.[35] The azidoformamidinium unit is not planar (torsion angle N11−C3−N7−N8 = 13.6(2)°) and the azide group is angulated (angle N7−N8−N9 = 171.1(1)°), which is quite common, for covalent azide groups due to hyperconjugation effects.[36] The amino groups of N10 and N11 building a planar fragment with the carbon atom C3 (angle N11−C3−N10 = 122.1(1)°).
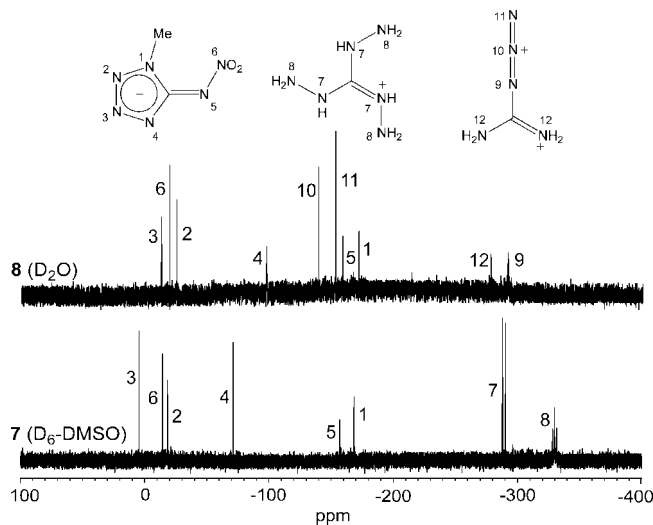
The three-dimensional structure of compound **8** is again significantly influenced by several hydrogen bonds. The molecular network contains one-dimensional, infinite chains as structural units. The nitrogen atoms of the azide group do not participate in any of the hydrogen bonds. The density of **8** (1.612 g cm^{-3}) is comparable to the density of bis(azidoformamidinium) 5,5′-azotetrazolate (1.624 g cm^{-3}), which had been recently investigated in this research group.[5a]

NMR Spectroscopy. Compounds **4−8** were investigated using ^{1}H, ^{13}C, and ^{15}N NMR (proton coupled) spectroscopy, and the chemical shifts are given with respect to TMS (^{1}H, ^{13}C) as well as MeNO$_2$ (^{15}N) as external standard. In all cases DMSO-d_6 or D$_2$O were used as the solvent. All recorded ^{1}H spectra show one signal caused by the protons of the methyl group (C2) at approximately 3.66 ppm. The proton signals of the cations are shifted to lower field in the range of 4.5−11 ppm. Two signals can be assigned in the ^{13}C spectra, caused by the methyl groups (ca. 33.1 ppm) and the low-field shifted tetrazole carbon atom (ca. 157.7 ppm). Since **7** and **8** have the highest nitrogen content within the investigated derivatives, the proton-coupled ^{15}N spectra in DMSO-d_6 (**7**) and D$_2$O (**8**), respectively, were recorded and are shown in Figure 8. The assignments of the signals are based on the analysis of the observed ^{15}N−^{1}H coupling constants and by comparison with literature.[37] The solvent shift of the ^{15}N signals to higher fields in D$_2$O can be clearly seen in Figure 8.

Vibrational Spectroscopy. **1** and the resulting salts **4−8** can be easily identified using vibrational spectroscopy (IR and Raman). The absorption band of the C=N stretching vibration is the most significant peak in the Raman spectrum of 1-methyl-5-nitriminotetrazole (**1**) and lies in the range from 1670 to 1580 cm^{-1}. This absorption band is shifted to

(34) Bracuti, A. J. *Acta Crystallogr.* **1979**, *B35*, 760−761.
(35) Müller, U.; Bärnighausen, H. *Acta Crystallogr.* **1970**, *26B*, 1671−1679.
(36) Klapötke, T. M. *Moderne Anorganische Chemie*, 3rd ed.; Riedel, E., Ed.; Walter de Gruyter, Berlin; **2007**; pp 84−86.
(37) Karaghiosoff, K.; Klapötke, T. M.; Meyer, P.; Piotrowski, H.; Polborn, K.; Willer, R. L.; Weigand, J. J. *J. Org. Chem.* **2006**, *71*, 1295−1305.
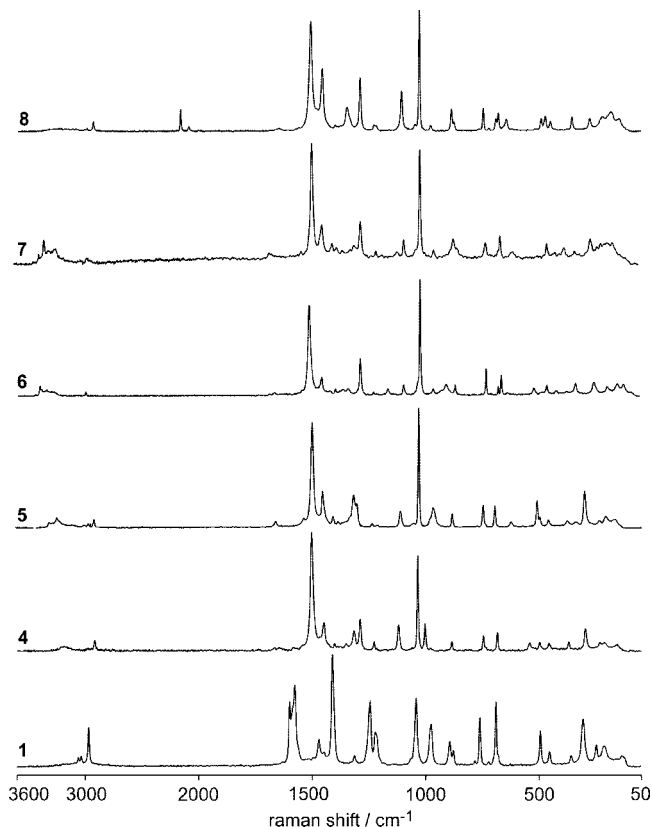
Figure 9. Raman spectra of 1-methyl-5-nitriminotetrazole (**1**) and its salts **4–8**.

Figure 10. DSC plots (endo down) of compounds **4–8** (5 °C min^{-1}). Melting points, T_{onset}: **4**, 192 °C; **5**, 154 °C; **6**, 120 °C; **7**, 158 °C; **8**, 118 °C. Temperature of decomposition, T_{onset}: **4**, 210 °C; **5**, 216 °C; **6**, 208 °C; **7**, 210 °C; **8**, 165 °C.

lower wavenumbers (1550–1500 cm^{-1}) for the deprotonated molecule and its salts. The Raman spectra for the compounds **4–8** are shown in Figure 9. It can be seen that the anions are much higher in intensity in comparison to the cations. The N–H stretch vibrations of the cations can only be obtained as weak absorption bands in the range from 3400 to 3200 cm^{-1}. Also the C–N and N–N stretching vibrations can be assigned to weak peaks ranging from 1700 to 1400 cm^{-1}. In the spectrum of **8** there are two absorption bands (2189 and 2112 cm^{-1}), which can be identified as ν_{sym} and ν_{asym}, respectively, of the covalent-bonded azide group. There are further characteristic absorption bands of the vibrations in the 1-methyl-5-nitriminotetrazolate anion, which were assigned by calculating (DFT B3LYP/cc-pVDZ) the spectra, after optimizing the geometry using the Gaussian 03 software:[38] 3080–3000 cm^{-1} [$\nu_{sym}(CH_3)$], 1560–1480 cm^{-1} [$\nu_{asym}(NO_2)$, $\upsilon(C=N)$], 1460–1400 cm^{-1} [$\nu_{asym}(CH_3)$], 1550–1350 cm^{-1} [$\nu(CN_4)$, $\upsilon(C-N)$], 1050–980 cm^{-1} [$\nu_{sym}(NNO_2)$], 1350–700 cm^{-1} [$\nu(NCN)$, $\nu(NN)$, $\gamma(CN)$, $\delta(CN_4)$].

Physicochemical Properties. As a result of the promising energetic characteristics of **4–8**, their physicochemical properties were investigated.

Differential Scanning Calorimetry (DSC). The thermal behavior of the 1-methyl-5-nitriminotetrazolate salts (**4– 8**) was determined, using DSC measurements. All DSC measurements were performed under constant nitrogen flow (20 mL min^{-1}) in covered Al containers with a hole (0.1 mm) for gas release
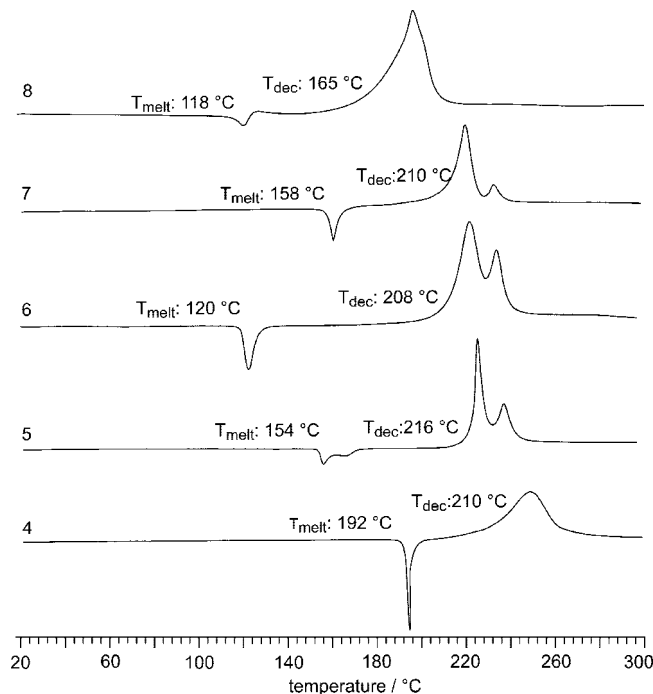
on a Linseis PT 10 DSC,[39] calibrated by pure indium and zinc standards at a heating rate of 5 °C min^{-1}. The thermal behavior of approximately 2 mg of the compounds **4–8** in the temperature range from 50 °C to 300 °C is illustrated as DSC plots in Figure 10. The melting points and the temperatures of decomposition are given as onset temperatures. The well-defined melting points depend on the number of hydrogen bonds, which can be found in the corresponding crystal structures. Compounds **6** and **8** melt at significantly lower temperatures (120° and 118 °C) than **4**, **5**, and **7** since the packing of the molecules within the crystal structure is only influenced by five and six hydrogen bonds, respectively. In contrast at least 10 hydrogen bonds can be found in the structures of **4** and **7** resulting in higher melting points (192 and 158 °C). Except for **8**, all salts decompose at temperatures slightly higher than 200 °C in a range from 208 to 216 °C. This is about 90 °C higher than the decomposition temperature of neutral **1**, which decomposes at 125 °C. It is also higher than the decomposition temperature of the ammonium salt (188 °C), and the influence of the deprotonation and the selection of the cation can be seen. The second decomposition of **5**, **6**, and **7** could not yet be investigated. The intensive endothermic point of **6** at 120 °C results both from the dehydration and also the melting of compound **6**. In contrast **8** decomposes at a temperature of 165 °C since it contains an azido group, which is more sensitive towards temperature.

All compounds seem to be long term stable at room temperature. This was tested using a TSC (thermal safety calorimetry) experiment in a RADEX V5 oven by heating **4–8** 50 °C below their decomposition temperatures for 48 h. After this time, the Raman spectra of all compounds were unaltered.

(38) Frisch, M. J.; et al. *Gaussian 03*, Revision A.1, Gaussian, Inc.: Pittsburgh, PA, 2003.
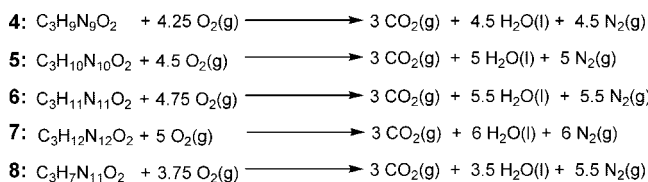
(39) http://www.linseis.com/.

Table 2. Physicochemical Properties of 1-Methyl-5-nitriminotetrazolate Salts 4–8

	4	**5**	**6**	**7**	**8**
formula	$C_3H_9N_9O_2$	$C_3H_{10}N_{10}O_2$	$C_3H_{11}N_{11}O_2$	$C_3H_{12}N_{12}O_2$	$C_3H_7N_{11}O_2$
molecular mass (g/mol)	206.16	218.18	233.19	248.21	229.16
impact sensitivity (J)[a]	40	10	7.5	6	4
friction sensitivity (N)[b]	>360	>360	>360	240	160
N (%)[c]	62.05	64.20	66.07	67.72	67.23
Ω (%)[d]	−66.94	66.00	−65.18	−64.46	−52.36
combustion	yes	yes	yes	yes	yes
$T_{dec.}$ (°C)[e]	210	216	208	210	165
ρ (g cm^{-3})[f]	1.550	1.57 (exp.)	1.61	1.57	1.61
$-\Delta_{comb}U$ (kJ g^{-1})[g]	12.95	13.18	13.36	14.45	11.34
$-\Delta_{comb}H$ (kJ mol^{-1})[h]	2622	2867	3105	3465	2586
$\Delta_fH_m°$ (kJ mol^{-1})[i]	155	257	352	569	405
$\Delta_fU°$ (kJ kg^{-1})[j]	885	1303	1667	2423	1876
			calculated values using EXPLO5		
$-\Delta_EU_m°$ (kJ kg^{-1})[k]	3656	3959	4224	4888	4174
T_E (K)[l]	2692	2805	2916	3210	3210
p (kbar)[m]	206	227	261	273	230
D (m s^{-1})[n]	7747	8062	8559	8770	7910
gas vol. [L kg^{-1}][o]	844	859	872	886	802

[a] BAM methods, see refs 38–44. [b] BAM methods, see refs 38–44. [c] Nitrogen content. [d] Oxygen balance. [e] Decomposition temperature from DSC (β = 5 °C). [f] Estimated from X-ray diffraction. [g] Experimental (constant volume) combustion energy. [h] Experimental molar enthalpy of combustion. [i] Molar enthalpy of formation. [j] Energy of formation. [k] Energy of explosion, EXPLO5 V5.02. [l] Explosion temperature. [m] Detonation pressure. [n] Detonation velocity. [o] Assuming only gaseous products, EXPLO5 V5.02.

Scheme 3. Combustion Equations of the Salts 4–8

4: $C_3H_9N_9O_2$ + 4.25 O_2(g) ⟶ 3 CO_2(g) + 4.5 H_2O(l) + 4.5 N_2(g)

5: $C_3H_{10}N_{10}O_2$ + 4.5 O_2(g) ⟶ 3 CO_2(g) + 5 H_2O(l) + 5 N_2(g)

6: $C_3H_{11}N_{11}O_2$ + 4.75 O_2(g) ⟶ 3 CO_2(g) + 5.5 H_2O(l) + 5.5 N_2(g)

7: $C_3H_{12}N_{12}O_2$ + 5 O_2(g) ⟶ 3 CO_2(g) + 6 H_2O(l) + 6 N_2(g)

8: $C_3H_7N_{11}O_2$ + 3.75 O_2(g) ⟶ 3 CO_2(g) + 3.5 H_2O(l) + 5.5 N_2(g)

Bomb Calorimetry. Bomb calorimetric measurements were performed using a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb for the combustion of high energetic materials.[40] Approximately 200 mg of the samples was pressed with a well-defined amount of benzoic acid (ca. 800 mg) to form a tablet to ensure better combustion. To ignite the sample a Parr 45C10 alloy fuse wire was used, and in all measurements a correction of 9.6 (IT) J cm^{-1} was applied. After each run the bomb was examined for evidence of non-combusted carbon, and the recorded data are the average of three single measurements. The calorimeter was calibrated by the combustion of certified benzoic acid (SRM, 39i, NIST) in an oxygen atmosphere at a pressure of 30.5 bar. The experimental results for the constant volume combustion energy (ΔU_c) of the 5-nitriminotetrazolate salts **4–8** are summarized in Table 2. On the basis of the formula $\Delta H_c = \Delta U_c + \Delta nRT$ ($\Delta n = \Delta n_i$ (products, g) − Δn_j (reactants, g); Δn_i is the total molar amount of gases in the products or reactants), the standard molar enthalpy of combustion ($\Delta H_c°$) can be derived. Using the combustion reactions in Scheme 3 and the Hess thermochemical cycle, the enthalpies of formation ($\Delta_fH°$) at 298.15 K were calculated. The heats of formation of the combustion products (carbon dioxide $\Delta_fH°_{298}(CO_{2(g)})$ =

-393.5 kJ mol^{-1}) and water ($\Delta_fH°_{298}(H_2O_{(g)}) = -241.8$ kJ mol^{-1}) were obtained from the literature.[41]

The results of the determination of the heats of formation for compounds **4–8** show their endothermic characters since the calculated values are all significantly positive. The heats of formation show the significant trend of increasing endothermicity for compounds **4–7**. The increase of the endothermic character is based on the compounds' rising nitrogen content and N–N single bonds in the row from the guanidinium to the triaminoguanidinium cation. This trend of **4–7** corresponds to the sensitivities of the investigated compounds. Solitary is the value of the azidoformamidinium derivative. $\Delta_fH°_{298}$ (kJ mol^{-1}): **4**, +155; **5**, +257; **6**, +352; **7**, +569; **8**, +405.

Sensitivities. The impact sensitivity tests was carried out according to STANAG 4489[42] modified according to instruction[43] using a BAM (Bundesanstalt für Materialforschung) drophammer.[44] The friction sensitivity tests were carried out according to STANAG 4487[45] modified according to instruction[46] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[47] Concerning the impact sensitivity compound **4** is "less

(40) Parr 1356 Isoperibol Bomb Calorimeter, Operating Instruction Manual No. 369M, Parr Instrument Company, Moline, Illinois (U.S.A.). http://www.parrinst.de/.

(41) (a) Wiberg, N. In *Lehrbuch der Anorganischen Chemie/Holleman-Wiberg*, 101st ed.; Walter de Gruyter, Berlin, **1995**, pp 250, 859, and 1176. (b) NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June **2005** Release. http://webbook.nist.gov/chemistry.

(42) *NATO standardization agreement (STANAG) on explosives, impact sensitivity tests*, no. 4489, 1st ed., Sept. 17, **1999**.

(43) WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, **2002**.

(44) http://www.bam.de.

(45) *NATO standardization agreement (STANAG) on explosive, friction sensitivity tests*, no. 4487, 1st ed., Aug. 22, **2002**.

(46) WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, **2002**.

(47) Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J. Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a.> 80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.

sensitive", while **5**, **6**, **7**, and **8** have to be classified as "sensitive" and therefore handled with special security measurements. In contrast, **4**−**6** are insensitive towards friction while **7** and **8** are again classified as "sensitive". With the trends of rising nitrogen content and heats of formation the sensitivities towards friction and impact are increased.

All salts were tested negative on their sensitivity against electrical discharge using a 20 kV tesla-coil spark device.

Detonation Parameters. The detonation parameters were calculated using the program EXPLO5 V5.02.[48] The program is based on the steady-state model of equilibrium detonation and uses Becker−Kistiakowsky−Wilson's equation of state (BKW E.O.S.) for gaseous detonation products and Cowan−Fickett E.O.S. for solid carbon.[49] The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated below the equations with X_i being the mole fraction of ith gaseous product and k_i the molar covolume of the ith gaseous product:[50]

$$pV/RT = 1 + xe^{\beta x} \qquad x = \left(\kappa \sum X_i k_i \right) / [V(T + \theta)]^a \tag{1}$$

$$a = 0.5, \quad \beta = 0.176, \quad k = 14.71, \quad \theta = 6620 \tag{2}$$

The calculations were performed using the maximum densities according to the crystal structures. Compound **7** is the most promising explosive since the detonation pressure (p_d = 273 kbar) and velocity (v_d = 8770 m s^{-1}) clearly exceed the calculated values for TNT (p_d = 202 kbar, v_d = 7150 m s^{-1}), which is still applied in military and civil sectors. The performance of **7** is even very similar compared to RDX (royal demolition explosive; p_d = 340 kbar, v_d = 8882 m s^{-1}), which was successfully introduced by the British Army and is usually used in military explosives.[51] Due to their lower nitrogen content and molar amount of gaseous reaction products, compounds **4**−**6** do not reach the level of **7** according the detonation pressure and velocity. Compound **6** is also promising since the higher density (1.61 g cm^{-1}) compared to **7** (1.57 g cm^{-1}) almost compensates the lower nitrogen content. There are only slight differences in the volume of gaseous decomposition products (**4**, 844; **5**, 859; **6**, 872; **7**, 886 L kg^{-1}), which are founded on the different detonation temperatures (**4**, 2692; **5**, 2805; **6**, 2916; **7**, 3210 K) and their influence on the Boudouard equilibrium.

Although the calculated values for **8** (p_d = 230 kbar, v_d = 7910 m s^{-1}) are also promising, a broad application is

excluded due to the high sensitivity towards friction and impact. The lower temperature of decomposition is also another disadvantage of **8**.

As **7** features the best calculated performance, acceptable density, and sensitivities, it is the most promising newly developed compound and therefore its experimental performance was tested using a "Koenen" test.

Koenen Test of Triaminoguanidinium 1-Methyl-5-nitriminitetrazolate. Compound **7** was investigated according to its explosion performance under confinement using a "Koenen test" steel sleeve apparatus.[52,53] The performance of the explosive can be related to the data obtained from the Koenen Test. Also the shipping classification of the substance can be determined and the degree of venting required to avoid an explosion during processing operations evaluated. The explosive is placed in a non-reusable open-ended flanged steel tube, which is locked up by a closing plate with variable orifice (0−10 mm), through which formed gaseous decomposition products are vented. A defined volume of 25 mL of the compound is loaded into the flanged steel tube, and a threaded collar is slipped onto the tube from below. The closing plate is fitted over the flanged tube and secured with a nut. The explosion is initiated via thermal ignition using four Bunsen burners, which are started simultaneously. The test is completed when either rupture of the tube or no reaction is observed, after heating the tube for a minimal time period of at least 5 min. In case of the tube's rupture the fragments are collected and weighed. The reaction is evaluated as an explosion if the tube is destroyed into three or more pieces. The Koenen test was performed with 27 g of triaminoguanidinium 1-methyl-5-nitriminotetrazolate using a closing plate with an orifice of 10 mm. The first trial was successful, indicated by the rupture of the steel tube into more than 15 fragments, which are shown in Figure 11. TNT destroys the steel sleeve up to an orifice width of 6 mm, RDX even up to 8 mm.[51] Compared to these applied explosives the performance of compound **7** is obviously better, although the calculated detonation parameters of RDX are slightly higher.

Conclusion

From the experimental study of N-rich 1-methyl-5-nitriminotetrazolate salts the following conclusions can be drawn:

1-Methyl-5-nitriminotetrazole can be easily deprotonated in aqueous solution using alkali hydroxides forming the corresponding alkali salts in nearly quantitative yields. These form the silver salt by the reaction with AgNO$_3$ in aqueous solutions.

The nitrogen-rich 1-methyl-5-nitriminotetrazolate salts **4**−**8** can easily be obtained via metathesis reactions using silver 1-methyl-5-nitriminotetrazolate and the guanidinium chlorides in aqueous solution with high yields and good purity. An alternative synthesis route is the reaction of guanidinium perchlorates with potassium 1-methyl-5-nit-

(48) (a) Suceska, M., EXPLO5.V2, Computer program for calculation of detonation parameters. *Proceediungs of the 32nd Int. Annual Conference of ICT*, July 3−6, **2001**, Karlsruhe, Germany, pp 110−111. (b) Suceska, M. *Proceedings of 30th Int. Annual Conference of ICT*, June 29−July 2, **1999**, Karlsruhe, Germany, 50/1.
(49) Suceska, M. *Propellants, Explos., Pyrotech.* **1991**, *16* (4), 197−202.
(50) (a) Sućeska, M. *Mater. Sci. Forum* **2004**, *465*−*466*, 325−330. (b) Sućeska, M. *Propellants, Explos., Pyrotech.* **1999**, *24*, 280−285. (c) Hobbs, M. L.; Baer, M. R. *Proceedings of the 10th Symp. (International) on Detonation*, ONR 33395-12, Boston, MA, July 12−16, **1993**; p 409.
(51) Köhler, J.; Meyer, R. *Explosivstoffe*, 9th ed.; Wiley-VCH: Weinheim, **1998**, pp 166−168.

(52) West, R. C.; Selby, S. M. *Handbook of Chemistry and Physics*, 48th ed.; The Chemical Rubber Co.: Cleveland, 1967, pp D22−D51.
(53) Ostrovskii, V. A.; Pevzner, M. S.; Kofman, T. P.; Tselinskii, I. V. *Targets Heterocycl. Syst.* **1999**, *3*, 467.
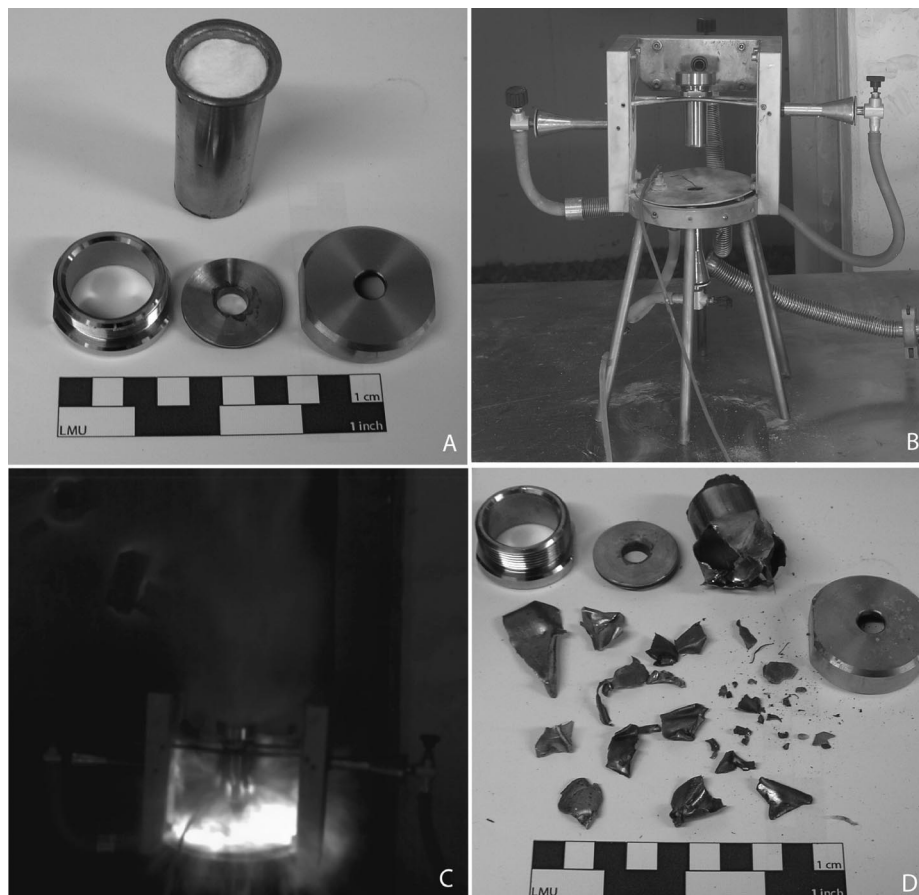
Figure 11. (A) Steel sleeve loaded with 27 g of **7**. (B) Koenen test setup showing four Bunsen burners. (C) Moment of explosion filmed using a high speed camera (2500 frames s^{-1}). (D) Result of the Koenen test showing the collected fragments.

riminotetrazolate. This route eliminates the light sensitive silver salt. **4**−**8** can be recrystallized from water/ethanol mixtures resulting in colorless crystals.

The crystal structures of **3**, **4**, **6**, **7**, and **8** were determined using low temperature single crystal diffraction showing similar geometry of the 1-methyl-5-nitriminotetrazolate anion. Only the constitution of the nitramine group is variable since the coordination of the anions via classical hydrogen bonds is different. The compounds crystallize in monoclinic (**3**, **4**, and **8**) or triclinic (**6** and **7**) space groups. **6** crystallizes as monohydrate, which can be dehydrated by heating under high-vacuum.

A comprehensive analytical characterization of the physicochemical properties and sensitivities of the endothermic compounds **4**−**8** is given. Although the salts are energetic materials with high nitrogen contents, they show good stabilities towards friction and impact and a good thermal stability. Especially **4**−**7** show well-defined melting points in the range from 120 to 195 °C, which are dependent on the number of existing hydrogen bonds and temperatures of decomposition over 200 °C.

Promising detonation parameters were calculated for **4**−**8** compared to common explosives like TNT and RDX. The performances (calculated values: $p_d = 273$ kbar; $v_d = 8770$ m s^{-1}) of triaminoguanidinium 1-methyl-5-nitriminotetrazolate (**7**) even successful in the Koenen test using a critical diameter of 10 mm qualifies it for further investigations concerning military applications.

Note Added in Proof. An improved synthesis for the promising energetic compound **7** was investigated. **7** is formed by the reaction of two equiv. of hydrazine hydrate with **5**, which is obtained by combining **1** with aminoguanidine bicarbonate. An overall yield of >82 % was recovered. See the last two paragraphs of the Experimental Section for further details.

Supporting Information Available: (1) Table of geometry (lengths, angles, torsion angles) data of the crystal structures (PDF) and (2) crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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