

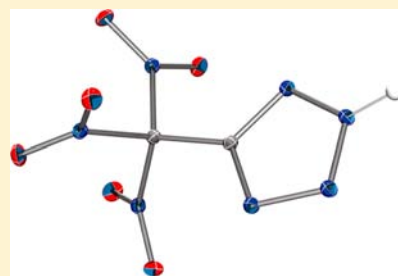
# Energetic High-Nitrogen Compounds: 5-(Trinitromethyl)-2H-tetrazole and -tetrazolates, Preparation, Characterization, and Conversion into 5-(Dinitromethyl)tetrazoles

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## S Supporting Information

**ABSTRACT:** A convenient access to 5-(trinitromethyl)-2H-tetrazole (HTNTz) has been developed, based on the exhaustive nitration of 1H-tetrazole-5-acetic acid, which was prepared from ethyl cyanoacetate and  $\text{HN}_3$  in a 1,3-dipolar cycloaddition reaction, followed by basic hydrolysis. HTNTz was converted into the ammonium, guanidinium, rubidium, cesium, copper, and silver 5-(trinitromethyl)-2H-tetrazolates. In addition, the ammonia adducts of the copper and silver salts were isolated. The reaction of HTNTz with hydrazine and hydroxylamine resulted in the formation of hydrazinium 5-(dinitromethyl)tetrazolate and hydroxylammonium 5-(dinitromethyl)-1H-tetrazolate, respectively. Acid treatment of both 5-(dinitromethyl)tetrazolates resulted in the isolation of 5-(dinitromethylene)-4,5-dihydro-1H-tetrazole, which was converted into potassium 5-(dinitromethyl)-1H-tetrazolate by reaction with  $\text{K}_2\text{CO}_3$ . All prepared compounds were fully characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ , and  $^{15}\text{N}$  NMR spectroscopy and X-ray crystal structure determination. Initial safety testing (impact, friction, and electrostatic sensitivity) and thermal stability measurements (differential thermal analysis, DTA) were also carried out. The 5-(trinitromethyl) and 5-(dinitromethyl)tetrazoles are highly energetic materials that explode upon impact or heating.



## INTRODUCTION

In energetic materials research, much effort has been devoted to the development of environmentally benign, “green” energetic materials.<sup>1</sup> Tetrazoles are readily accessible nitrogen-rich energetic compounds. The oxygen balance of a molecule and its potential usefulness as an energetic material can be increased by the introduction of nitro functionalities. 5-Nitro-2H-tetrazole (HNT) and salts with the related 5-nitrotetrazolate anion ( $\text{NT}^-$ ) are well-known and have attracted much interest as primary explosives and energetic materials.<sup>2–9</sup> Dinitromethyltetrazole was discovered in 1964, and salts of its anion have been the subject of studies for many years.<sup>10–19</sup> The synthesis of 5-(trinitromethyl)-2H-tetrazole (HTNTz) **4** by reaction of trinitroacetonitrile **3** and trimethylsilyl azide has been reported, but the obtained product was described as an orange-yellow oil that evolved nitrogen oxides on prolonged standing at ambient temperatures and was successively converted into the ammonium salt.<sup>20</sup> In a later report, HTNTz **4** was not isolated or fully characterized but has been prepared as an intermediate by the reaction of trinitroacetonitrile **3** with hydrogen azide and was immediately converted into the tetrabutylammonium salt.<sup>21</sup>

In this Article, we communicate an improved synthesis and X-ray crystallographic characterization of 5-(trinitromethyl)-2H-tetrazole (HTNTz), which had previously been obtained only as an impure oil and several energetic salts with the 5-(trinitromethyl)tetrazolate anion. In addition, we report the preparation of several 5-(dinitromethyl)tetrazolates from HTNTz, as well as their X-ray crystal structures.

## EXPERIMENTAL SECTION

**Caution!** Most compounds of this work are energetic materials that can explode under certain conditions (e.g., elevated temperatures, impact, friction, or electric discharge). On several occasions, cesium and rubidium 5-(trinitromethyl)tetrazolate even exploded upon crystallization. A mixture of anhydrous hydrazine and neat 5-(trinitromethyl)-2H-tetrazole is hypergolic: mixing both compounds results in an instantaneous fire. Appropriate safety precautions,<sup>22</sup> such as the use of shields or barricades in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves and suits made from leather and/or Kevlar) should be taken all the time when handling these materials. **Ignoring safety precautions may lead to serious injuries!**

**Materials and Apparatus.** All chemicals and solvents were obtained from Sigma–Aldrich or Alfa Aesar and were used as supplied. NMR spectra were recorded at 298 K on Bruker AMX500 or Varian VNMRS-600s spectrometers in  $(\text{CD}_3)_2\text{CO}$  or  $\text{D}_2\text{O}$  solutions in standard 5 mm glass tubes. Chemical shifts are given relative to neat tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or neat  $\text{CH}_3\text{NO}_2$  ( $^{14}\text{N}$ ,  $^{15}\text{N}$ ); br = broad; sh = shoulder; s = singlet. Raman spectra were recorded at ambient temperatures in Pyrex glass tubes in the range  $4000\text{--}80\text{ cm}^{-1}$  on a Bruker Equinox 55 FT-RA spectrometer using a Nd:YAG laser at 1064 nm or a Cary 83 spectrometer using an Ar laser at 488 nm. Infrared spectra were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  on Midac, M Series or Bruker Optics Alpha FT-IR spectrometers by use of KBr pellets. The pellets were prepared very carefully on an Econo minipress (Barnes Engineering Co.). Differential thermal analysis (DTA) curves were recorded with a purge of dry nitrogen gas on an OZM Research DTA552-Ex instrument with Meavy 2.2.0 software. The

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heating rate was 5 °C/min and the sample size was 3–15 mg. The impact and friction sensitivity data were determined on an OZM Research BAM fall hammer BFH-10 and an OZM Research BAM friction apparatus FSKM-10, respectively, through five individual measurements that were averaged. Both instruments were calibrated with RDX.

**Synthesis of Ethyl 2-(1*H*-Tetrazol-5-yl)acetate (1).**<sup>23,24</sup> A solution of ethyl cyanoacetate (69.0 g, 0.62 mol), ammonium chloride (35.4 g, 0.66 mol), and sodium azide (43.0 g, 0.66 mol) in dimethyl formamide (600 mL) was heated under nitrogen to 100 °C for 16 h. The obtained orange solution with some off-white precipitate was allowed to cool to ambient temperature and the solvent was removed under vacuum in a rotary evaporator. The orange residue was dissolved in water (200 mL) and acidified with 5 M hydrochloric acid solution. After a short while crystals started to form, and eventually the mixture took on a gel-like consistency. The off-white solid was filtered off by use of a Buchner funnel. Recrystallization from an ethanol/water mixture gave colorless crystals of ethyl 2-(1*H*-tetrazol-5-yl)acetate (49.0 g). Theoretical mass expected for 0.62 mol of C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> = 96.8 g (yield = 50.6%). DTA (5 °C·min<sup>-1</sup>) 124.4 °C melting. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, ppm) δ 1.21 t, <sup>3</sup>J(HH) = 7.3 Hz (CH<sub>2</sub>CH<sub>3</sub>); 3.4 br s (CN<sub>4</sub>H); 4.16 s (CH<sub>2</sub>CN<sub>4</sub>H); 4.17 q, <sup>3</sup>J(HH) = 7.3 Hz (CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, ppm) δ 14.4 (CH<sub>3</sub>CH<sub>2</sub>), 30.5 (CH<sub>2</sub>CO<sub>2</sub>Et), 62.3 (CH<sub>3</sub>CH<sub>2</sub>), 168.5 (CN<sub>4</sub>H). <sup>14</sup>N NMR (acetone-*d*<sub>6</sub>, ppm) δ -12, τ<sub>1/2</sub> = 870 Hz. Raman (1064 nm, 80 mW) ν (cm<sup>-1</sup>) = 2978 (7.5), 2942 (10.0), 2915 (2.3), 2876 (1.8), 2779 (0.2), 2732 (0.2), 1751 (1.5), 1686 (0.1), 1567 (0.6), 1551 (0.2 sh), 1483 (0.3), 1456 (1.3), 1397 (0.9), 1384 (0.7), 1372 (0.5 sh), 1339 (1.1), 1259 (1.1), 1219 (0.3), 1201 (0.5), 1164 (0.1), 1113 (0.9), 1091 (1.5), 1052 (1.0), 1008 (0.1), 949 (0.5), 885 (1.5), 789 (0.2), 727 (0.1), 713 (0.6), 687 (0.4), 630 (0.1), 568 (0.6), 422 (0.1), 358 (0.2), 339 (2.0), 310 (0.7), 300 (0.4 sh), 211 (0.3), 169 (4.5). IR (KBr): ν (cm<sup>-1</sup>) = 3473 (m), 3132 (m), 3022 (m sh), 2997 (s sh), 2987 (s), 2974 (s sh), 2941 (m sh), 2911 (s sh), 2871 (m sh), 2798 (m sh), 2733 (m sh), 2688 (m sh), 2611 (w sh), 2462 (vw sh), 1745 (vs), 1703 (w), 1567 (m), 1480 (m), 1454 (m), 1438 (mw), 1395 (s), 1382 (s), 1333 (s), 1249 (m), 1220 (s), 1199 (vs), 1161 (w sh), 1105 (m), 1051 (s), 1034 (s), 942 (s), 882 (m br), 807 (vw), 787 (m), 723 (w), 711 (w), 684 (m), 565 (m), 453 (vw), 422 (w).

**Synthesis of 1*H*-Tetrazole-5-acetic Acid (2).**<sup>24</sup> Ethyl 2-(1*H*-tetrazol-5-yl)acetate (45.2 g, 0.29 mol) and sodium hydroxide (45 g, 1.13 mol) were dissolved in water (1000 mL) and the solution was heated under reflux for 4 h. After the solution was allowed to cool to ambient temperature, it was acidified to pH 2 with 5 M hydrochloric acid solution and taken to dryness on a rotary evaporator. The off-white residue was extracted four times with hot acetonitrile (75 mL each). The combined acetonitrile phases were taken to dryness on the rotary evaporator. The white residue was recrystallized from acetonitrile. Colorless crystals of 1*H*-tetrazole-5-acetic acid (2) (35.1 g) were obtained. Theoretical mass expected for 0.29 mol of C<sub>3</sub>H<sub>4</sub>N<sub>4</sub>O<sub>2</sub> = 37.1 g (yield = 94.5%). DTA (5 °C·min<sup>-1</sup>) 167.1 °C melting. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, ppm) δ 4.15 s (CH<sub>2</sub>CN<sub>4</sub>H); 6.2 br s (CO<sub>2</sub>H) and (CN<sub>4</sub>H). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, ppm) δ 30.2 s (CH<sub>2</sub>CO<sub>2</sub>H); 151.7 s (CN<sub>4</sub>H); 169.5 s (CO<sub>2</sub>H). <sup>14</sup>N NMR (acetone-*d*<sub>6</sub>, ppm) δ -12, τ<sub>1/2</sub> = 800 Hz (CN<sub>4</sub>H). Raman (1064 nm, 80 mW) ν (cm<sup>-1</sup>) = 2978 (4.7), 2940 (10.0), 1744 (0.4), 1728 (2.2), 1565 (1.7), 1549 (0.5 sh), 1451 (90.6), 1441 (0.4 sh), 1420 (0.6), 1389 (0.7), 1354 (1.7), 1318 (1.3), 1260 (0.6), 1219 (0.8), 1192 (0.4), 1123 (0.6), 1105 (2.0), 1063 (1.4), 1019 (0.1), 949 (0.1), 918 (2.1), 786 (0.6), 724 (0.1), 698 (0.9), 664 (1.3), 575 (0.1), 545 (0.6), 413 (2.2), 361 (0.1), 344 (0.4), 290 (2.9), 196 (0.7), 169 (5.8), 133 (2.3). IR (KBr) ν (cm<sup>-1</sup>) = 1737 (vs), 1695 (w sh), 1563 (s), 1549 (w sh), 1451 (m), 1441 (m), 1423 (w sh), 1382 (s), 1351 (w), 1315 (m), 1263 (m), 1220 (m sh), 1200 (vs), 1121 (vw), 1099 (w), 1066 (m br), 1014 (w), 947 (m), 899 (m nr), 865 (m br), 813 (vw sh), 785 (w), 721 (w), 705 (vw), 698 (w), 662 (vs), 599 (vw sh), 574 (vw), 545 (vw), 453 (w br), 411 (s).

**Synthesis of Trinitroacetonitrile (3).**<sup>21,25</sup> Under an atmosphere of nitrogen, a mixture of cyanoacetamide (8.401 g, 0.1 mol) and tetrachloromethane (25 mL) was cooled to 0 °C. While the mixture

was stirring vigorously, 100% nitric acid (16 mL) was added through an addition funnel within a time period of 2 min. The cyanoacetamide dissolved and a yellow two-layer mixture was obtained. The mixture was cooled to -20 °C and oleum (20% SO<sub>3</sub>) (19 mL) was added within a time period of 2 min. The temperature was now raised to 0 °C, and the mixture was stirred for 2 h at this temperature and for an additional 8 h at ambient temperature. The pale yellow two-phase mixture was transferred into a separatory funnel and the upper organic layer was removed. The lower acidic layer was extracted three times with tetrachloromethane (15 mL each). The combined organic layers were extracted twice with cold (-5 °C) concentrated sulfuric acid (10 mL each), and the obtained colorless solution was kept over magnesium sulfate. Because of the reported instability of trinitroacetonitrile,<sup>25</sup> no efforts were made to isolate the neat compound. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) δ 103.4 (CN); 112.1 septet, <sup>1</sup>J(<sup>13</sup>C<sup>14</sup>N) = 9.5 Hz [C(NO<sub>2</sub>)<sub>3</sub>]. <sup>14</sup>N NMR (CDCl<sub>3</sub>, ppm) δ -45.4, τ<sub>1/2</sub> = 20 Hz (NO<sub>2</sub>); -88.3, τ<sub>1/2</sub> = 320 Hz (CN).

**Synthesis of 5-(Trinitromethyl)-2*H*-tetrazole (4).** *Method 1.*<sup>21</sup> Acetic acid (150 mL) was added to a stirred suspension of sodium azide (6.5 g, 0.10 mol) in tetrachloromethane (140 mL) at 0 °C. After 2–3 min, the temperature was lowered to -25 °C and a solution of trinitroacetonitrile (0.1 mol) in tetrachloromethane (45 mL) (prepared as described above) was slowly added at a speed so that the temperature never rose above -15 °C. When the addition was complete, the yellow reaction mixture was kept at -25 °C for an additional 15 min before the temperature was raised to ambient temperature. The mixture was stirred at ambient temperature for 8 h and then taken to dryness on a rotary evaporator. The tacky yellow residue was dissolved in a mixture of dichloromethane (30 mL) and 1 M sulfuric acid (5 mL). The organic phase was separated and the aqueous layer was extracted three times with dichloromethane (5 mL each). The combined organic phases were dried over magnesium sulfate and taken to dryness on a rotary evaporator. The colorless, oily residue solidified to a crystalline solid after 8 h of pumping in a vacuum at ambient temperature. 5-(Trinitromethyl)-2*H*-tetrazole (4) was obtained as colorless crystals (14.0 g). Theoretical mass expected for 0.10 mol of C<sub>2</sub>HN<sub>7</sub>O<sub>6</sub> = 21.9 g (yield = 63.7% based on cyanoacetamide).

*Method 2.* 1*H*-Tetrazole-5-acetic acid (10.0 g, 78.1 mmol) was slowly added to a cooled and well-stirred mixture of 98% sulfuric acid (64 mL) and 100% nitric acid (52 mL) at 0 °C during the course of 1 h. The temperature was slowly raised to ambient temperature over a period of 2 h, and the mixture was stirred for an additional 8 h at this temperature. The light yellow solution was carefully poured onto crushed ice (250 g) and the obtained solution was extracted four times with dichloromethane (100 mL each). The combined organic phases were dried over magnesium sulfate and filtered, and the solvent was evaporated at ambient temperature in a vacuum. Initially, a yellow oil was obtained that eventually solidified in a vacuum. 5-(Trinitromethyl)-2*H*-tetrazole (4) was obtained as a pale yellow solid (10.2 g). Theoretical mass expected for 78.1 mmol of C<sub>2</sub>HN<sub>7</sub>O<sub>6</sub> = 17.1 g (yield = 59.7%). DTA (5 °C·min<sup>-1</sup>) 100.9 °C explosion. <sup>1</sup>H NMR (5% C<sub>6</sub>D<sub>6</sub> in acetone, ppm) δ 14.1 s, τ<sub>1/2</sub> = 150 Hz (CN<sub>4</sub>H). <sup>13</sup>C NMR (5% C<sub>6</sub>D<sub>6</sub> in acetone, ppm) δ 122.5 septet, <sup>1</sup>J(<sup>13</sup>C<sup>14</sup>N) = 7.6 Hz [C(NO<sub>2</sub>)<sub>3</sub>]; 152.8 s (CN<sub>4</sub>H). <sup>14</sup>N NMR (5% C<sub>6</sub>D<sub>6</sub> in acetone, ppm) δ -35.6, τ<sub>1/2</sub> = 6 Hz (NO<sub>2</sub>); δ -47.0, τ<sub>1/2</sub> = 700 Hz (CN<sub>4</sub>H). <sup>15</sup>N NMR (5% C<sub>6</sub>D<sub>6</sub> in acetone, ppm) δ -35.7 s (NO<sub>2</sub>); δ -53.8 s, τ<sub>1/2</sub> = 15 Hz (CN<sub>4</sub>H). Raman (1064 nm, 45 mW) ν (cm<sup>-1</sup>) = 3200–2800 (0.4), 1628 (1.0), 1620 (1.9), 1610 (1.9), 1492 (3.0), 1456 (3.1), 1366 (0.6), 1351 (1.0), 1334 (0.8), 1282 (2.0), 1256 (1.4), 1236 (1.2), 1134 (3.5), 1108 (0.6), 1035 (0.4), 986 (0.8), 967 (2.0), 949 (2.2), 846 (3.0), 800 (0.4), 745 (0.4), 681 (0.6), 639 (0.7), 623 (0.7), 427 (2.0), 400 (3.5), 376 (3.8), 357 (8.0), 340 (3.2), 228 (0.4), 208 (0.6), 179 (1.1), 140 (5.7 sh), 128 (10.0). IR (KBr) ν (cm<sup>-1</sup>) = 3441 (m, br), 3060 (m, br), 2894 (m, br), 2777 (m, br), 1610 (vs), 1489 (v), 1455 (v), 1436 (v), 1394 (vw), 1332 (m), 1311 (m), 1280 (s), 1255 (vw, sh), 1238 (w), 1189 (m), 1132 (m), 1102 (w), 1038 (m), 985 (m), 947 (vw), 863 (w), 844 (m), 803 (s), 742 (m), 697 (vw), 680 (w), 637 (w), 622 (w).

**Synthesis of Ammonium 5-(Trinitromethyl)tetrazolate (5).** 5-(Trinitromethyl)-2H-tetrazole (0.438 g, 2.00 mmol) was dissolved in water (5 mL), and 30% aqueous ammonium hydroxide solution (5 mL) was added. The resulting pale yellow solution was taken to dryness at ambient temperature on a rotary evaporator. Ammonium 5-(trinitromethyl)tetrazolate (**5**) was isolated as colorless crystals (0.465 g). Theoretical mass expected for 2.00 mmol of  $C_2H_4N_8O_6$  = 0.472 g (yield = 98.5%). DTA (5 °C·min<sup>-1</sup>) 115.7 °C explosion. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm)  $\delta$  7.56 q, <sup>1</sup>J(<sup>1</sup>H<sup>14</sup>N) = 59.4 Hz (NH<sub>4</sub>). <sup>13</sup>C NMR (D<sub>2</sub>O, ppm)  $\delta$  126.2 s [C(NO<sub>2</sub>)<sub>3</sub>]; 152.0 s (CN<sub>4</sub>). <sup>14</sup>N NMR (D<sub>2</sub>O ppm)  $\delta$  -32.1,  $\tau_{1/2}$  = 8 Hz (NO<sub>2</sub>);  $\delta$  -61,  $\tau_{1/2}$  = 650 Hz (CN<sub>4</sub>); -361.8 quint, <sup>1</sup>J(<sup>14</sup>N<sup>1</sup>H) = 60.1 Hz (NH<sub>4</sub>). Raman (1064 nm, 45 mW)  $\nu$  (cm<sup>-1</sup>) = 3200–2800 (2.5), 1712 (0.4), 1621 (3.0), 1612 (1.5), 1598 (1.5), 1470 (0.6), 1435 (10.0), 1391 (0.7), 1358 (1.7), 1292 (1.4), 1207 (1.7), 1165 (0.6), 1110 (2.9), 1073 (3.5), 1022 (0.3), 992 (3.2 m), 966 (1.5 sh), 953 (3.4), 845 (8.1), 822 (0.5), 801 (0.6), 691 (0.9), 641 (0.7), 618 (1.0), 436 (2.5), 386 (5.8), 372 (5.0), 361 (9.0), 347 (3.5 sh), 341 (3.7), 229 (1.5), 212 (3.0), 198 (2.9), 160 (5.1 sh), 141 (9.0 sh), 131 (9.8), 113 (7.5). IR (KBr)  $\nu$  (cm<sup>-1</sup>) = 3424 (s br), 3203 (s), 3181 (s), 3136 (m), 3060 (s br), 3000 (s br), 2925 (m), 2883 (s), 2182 (w), 2128 (w), 1945 (w), 1699 (m), 1625 (vs), 1606 (vs), 1589 (vs), 1460 (s), 1443 (s), 1392 (m), 1357 (w), 1333 (w), 1315 (w), 1286 (m), 1228 (vw), 1205 (vw), 1163 (w), 1107 (m), 1070 (vw), 1052 (vw), 989 (m), 960 (w br), 844 (s), 805 (s), 800 (s), 736 (w), 688 (w), 640 (m), 615 (m), 596 (m), 451 (m).

**Synthesis of Guanidinium, Rubidium, and Cesium 5-(Trinitromethyl)tetrazolates (6–8).** A solution of 5-(trinitromethyl)-2H-tetrazole (0.438 g, 2.00 mmol) in acetone (5 mL) was added to a stirred suspension of guanidinium, rubidium, or cesium carbonate (5.0 mmol) in acetone (5 mL). Immediately, carbon dioxide gas was evolved and the solution turned yellow. After 30 min, the solution was filtered through a Buchner funnel and the solid was washed with some acetone. The solvent was evaporated from the filtrate in a stream of nitrogen.

**Guanidinium 5-(Trinitromethyl)tetrazolate (6).** Pale yellow crystals (0.525 g), theoretical mass expected for 2.00 mmol of  $C_3H_6N_{10}O_6$  = 0.556 g (yield = 94.5%). DTA (5 °C·min<sup>-1</sup>) 115.5 °C explosion. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm)  $\delta$  6.9 (CN<sub>3</sub>H<sub>6</sub>). <sup>13</sup>C NMR (D<sub>2</sub>O, ppm)  $\delta$  125.4 s [C(NO<sub>2</sub>)<sub>3</sub>]; 150.9 s (CN<sub>4</sub>); 155.3 s (CN<sub>3</sub>H<sub>6</sub>). <sup>14</sup>N NMR (D<sub>2</sub>O ppm)  $\delta$  -31.2 s,  $\tau_{1/2}$  = 20 Hz (NO<sub>2</sub>);  $\delta$  -65,  $\tau_{1/2}$  = 800 Hz (CN<sub>4</sub>); -308,  $\tau_{1/2}$  = 900 Hz (CN<sub>3</sub>H<sub>6</sub>). Raman (1064 nm, 100 mW)  $\nu$  (cm<sup>-1</sup>) = 1619 (1.1), 1444 (7.3), 1368 (1.5), 1368 (1.5 br), 1210 (1.1), 1179 (0.7), 1114 (1.5), 1068 (2.0), 1017 (9.5), 969 (2.0), 960 (1.7), 851 (5.4), 836 (1.6 sh), 623 (0.7), 534 (2.2), 523 (1.3), 450 (0.8), 423 (0.8), 408 (1.1), 362 (10.0), 349 (3.1 sh), 324 (1.1), 286 (0.7), 221 (1.6).

**Rubidium 5-(Trinitromethyl)tetrazolate (7).** Pale yellow crystals (0.608 g), theoretical mass expected for 2.00 mmol of  $C_2N_8O_6Rb$  = 0.607 g (quantitative yield). DTA (5 °C·min<sup>-1</sup>) 119.6 °C explosion. <sup>13</sup>C NMR (D<sub>2</sub>O, ppm)  $\delta$  125.9 s [C(NO<sub>2</sub>)<sub>3</sub>]; 152.0 s (CN<sub>4</sub>). <sup>14</sup>N NMR (D<sub>2</sub>O ppm)  $\delta$  -32.4,  $\tau_{1/2}$  = 10 Hz (NO<sub>2</sub>);  $\delta$  -62,  $\tau_{1/2}$  = 650 Hz (CN<sub>4</sub>). Raman (1064 nm, 35 mW)  $\nu$  (cm<sup>-1</sup>) = 1622 (3.0), 1605 (1.5), 1593 (0.8), 1434 (10.0), 1399 (1.5), 1368 (1.4), 1334 (0.2), 1316 (0.7), 1301 (1.0), 1289 (1.0), 1191 (1.0), 1147 (0.5), 1104 (2.4), 1044 (1.6 sh), 1037 (1.5 sh), 1018 (0.1), 992 (2.5), 951 (4.7), 849 (5.9), 804 (1.2), 739 (0.4), 680 (0.6), 648 (0.5), 622 (0.6), 431 (2.2), 391 (4.6), 375 (2.9), 360 (7.6), 348 (4.0), 226 (1.5 sh), 216 (2.1), 164 (6.1 sh), 158 (6.6), 132 (5.6). IR (KBr)  $\nu$  (cm<sup>-1</sup>) = 2959 (vw), 2926 (w br), 2903 (vw sh), 2859 (w), 2470 (vw), 2428 (vw), 2176 (vw sh), 2169 (vw), 2152 (vw), 2069 (vw), 2057 (vw), 1616 (vs sh), 1595 (vs), 1433 (m), 1395 (w), 1384 (m), 1365 (vw sh), 1313 (s sh), 1296 (s sh), 1285 (s), 1233 (vw), 1188 (w), 1143 (w), 1126 (vw), 1102 (m), 1040 (w), 1035 (w), 1017 (vw), 990 (m), 948 (w), 846 (s), 803 (vs), 738 (w), 731 (w), 599 (w sh), 677 (w), 644 (m), 617 (m), 489 (vw), 453 (m br).

**Cesium 5-(Trinitromethyl)tetrazolate (8).** Pale yellow crystals (0.691 g), theoretical mass expected for 2.00 mmol of  $C_2CsN_7O_6$  = 0.702 g (yield = 98.4%). DTA (5 °C·min<sup>-1</sup>) 129.9 °C explosion. <sup>13</sup>C NMR (D<sub>2</sub>O, ppm)  $\delta$  125.7 s [C(NO<sub>2</sub>)<sub>3</sub>]; 152.4 s (CN<sub>4</sub>). <sup>14</sup>N NMR (D<sub>2</sub>O ppm)  $\delta$  -31.7,  $\tau_{1/2}$  = 10 Hz (NO<sub>2</sub>);  $\delta$  -62,  $\tau_{1/2}$  = 600 Hz

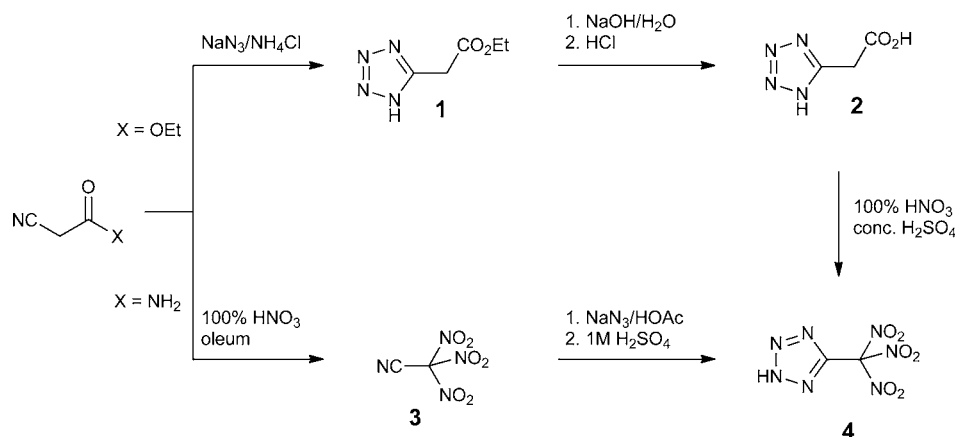
(CN<sub>4</sub>). Raman (1064 nm, 35 mW):  $\nu$  (cm<sup>-1</sup>) = 1636 (2.0), 1610 (0.8), 1442 (10.0), 1412 (0.5), 1370 (1.2), 1299 (1.5), 1289 (1.0 sh), 1150 (1.8), 1145 (0.5 sh), 1082 (4.2), 1000 (3.2), 951 (4.7), 882 (7.2), 812 (1.9), 652 (0.8), 453 (2.8), 370 (4.6), 352 (7.6), 324 (5.6), 232 (2.7), 172 (3.7 sh), 163 (5.9), 125 (4.5). IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2961 (w sh), 2921 (m sh), 2897 (m br), 2853 (w sh), 2457 (w), 2423 (vw), 2242 (vw), 2209 (vw), 2175 (w), 2165 (vw), 2062 (vw), 2048 (vw), 1619 (vs), 1604 (vs), 1588 (vs), 1429 (m), 1393 (m), 1364 (vw sh), 1314 (s), 1297 (s), 1284 (s), 1235 (vw sh), 1186 (w), 1143 (w), 1099 (m), 1038 (w), 987 (m), 982 (m sh), 946 (w), 845 (s), 802 (vs), 737 (w), 731 (w), 704 (w), 675 (m), 644 (m), 619 (m), 599 (vw sh), 452 (w).

**Synthesis of Silver 5-(Trinitromethyl)tetrazolate (9).** A solution of silver nitrate (0.425 g, 2.50 mmol) in water (5 mL) was added to a solution of 5-(trinitromethyl)-2H-tetrazole (0.438 g, 2.00 mmol) in water (5 mL). The pale yellow precipitate was filtered off, washed with water, and dried in the air. Silver 5-(trinitromethyl)tetrazolate (**9**) was obtained as a pale yellow solid (0.626 g). Theoretical mass expected for 2.00 mmol of  $C_2AgN_7O_6$  = 0.604 g (quantitative yield). DTA (5 °C·min<sup>-1</sup>) 123.4 °C explosion. Recrystallization from 30% ammonium hydroxide solution resulted in isolation of the ammonia adduct (**9a**) [Ag(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[C<sub>12</sub>Ag<sub>4</sub>N<sub>42</sub>O<sub>36</sub>] as pale yellow crystals. DTA (5 °C·min<sup>-1</sup>) 122.8 °C explosion. Raman (1064 nm, 30 mW)  $\nu$  (cm<sup>-1</sup>) = 3200–2850 (2.0), 1615 (1.0), 1452 (7.5 sh), 1444 (10.0), 1283 (1.0), 1218 (2.5), 1177 (1.0), 1115 (4.0), 1090 (1.5), 1062 (0.8), 1043 (1.0), 993 (3.7), 970 (1.1), 960 (2.0), 946 (0.7), 846 (8.1), 428 (2.2), 404 (1.1), 363 (9.0), 321 (0.6), 309 (1.2), 214 (1.5), 151 (4.5 sh), 135 (6.0).

**Synthesis of Copper 5-(Trinitromethyl)tetrazolate (10).** A solution of copper sulfate pentahydrate (0.375 g, 1.50 mmol) in water (5 mL) was added to a solution of 5-(trinitromethyl)-2H-tetrazole (0.438 g, 2.00 mmol) in water (5 mL). The blue precipitate was filtered off, washed with water, and dried in air. Copper 5-(trinitromethyl)tetrazolate (**10**) was obtained as a blue solid (0.541 g). Theoretical mass expected for 1.00 mmol of  $C_4CuN_{14}O_{12}$  = 0.500 g. DTA (5 °C·min<sup>-1</sup>): 122.8 °C explosion. Recrystallization from 30% ammonium hydroxide solution resulted in isolation of the ammonia adduct (**10a**) as dark blue crystals (0.519 g). Theoretical mass expected for 1.00 mmol of  $C_4H_9CuN_{17}O_{12} \cdot 3NH_3$  = 0.551 g (94.2%). DTA (5 °C·min<sup>-1</sup>) 117.3 °C explosion. Raman (1064 nm, 35 mW)  $\nu$  (cm<sup>-1</sup>) = 3300–2900 (0.5), 1610 (1.7), 1456 (10.0), 1369 (1.1), 1275 (2.5), 1155 (1.3), 1078 (1.5), 993 (6.0), 966 (2.8), 847 (7.0), 611 (0.8), 482 (1.0), 432 (1.9), 364 (8.2). IR (KBr)  $\nu$  (cm<sup>-1</sup>) = 2964 (w br), 2927 (w br), 2901 (w br), 1600 (vs), 1387 (w), 1340 (vw sh), 1281 (s), 1238 (w), 1141 (w sh), 1104 (m), 1082 (w), 991 (m), 844 (s), 800 (s), 741 (w), 675 (vw), 645 (w), 623 (w), 593 (w), 458 (m).

**Synthesis of Hydroxylammonium 5-(Dinitromethyl)-1H-tetrazolate (11).** An aqueous solution of 50% hydroxylamine (2.0 g, 61 mmol) was slowly added to a solution of 5-(trinitromethyl)-2H-tetrazole (0.438 g, 2.00 mmol) in water (5 mL). After gas evolution ceased, the yellow solution was taken to dryness by a stream of nitrogen and the yellow residue was recrystallized from water. Hydroxylammonium 5-(dinitromethyl)-1H-tetrazolate (**11**) was obtained as yellow crystals (0.379 g). Theoretical mass expected for 2.00 mmol of  $C_2H_5N_7O_5$  = 0.414 g (yield = 91.6%). DTA (5 °C·min<sup>-1</sup>) 149.9 °C explosion. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm)  $\delta$  3.98 br (NH<sub>3</sub>OH and CN<sub>4</sub>H). <sup>13</sup>C NMR (D<sub>2</sub>O, ppm)  $\delta$  129.0 br s [C(NO<sub>2</sub>)<sub>2</sub>]; 156.3 s (CN<sub>4</sub>). <sup>14</sup>N NMR (D<sub>2</sub>O ppm)  $\delta$  -24.6,  $\tau_{1/2}$  = 110 Hz (NO<sub>2</sub>);  $\delta$  -68,  $\tau_{1/2}$  = 850 Hz (CN<sub>4</sub>); -291,  $\tau_{1/2}$  = 500 Hz (NH<sub>3</sub>OH). Raman (1064 nm, 40 mW)  $\nu$  (cm<sup>-1</sup>) = 3230–3065 (1.4), 3010–2800 (1.5), 2889 (1.2), 1593 (0.7), 1515 (1.8), 1486 (4.3), 1425 (6.8), 1376 (7.5), 1338 (1.5), 1243 (1.7), 1222 (4.1), 1200 (1.2), 1164 (6.7), 1126 (10.0), 1087 (0.9), 1022 (6.7), 993 (3.4), 838 (6.4), 820 (1.7), 778 (1.5), 759 (1.1), 471 (4.4), 445 (2.9), 415 (1.3), 326 (2.0), 291 (3.3), 248 (3.3), 203 (1.6). IR (KBr)  $\nu$  (cm<sup>-1</sup>) = 3448 (m br), 3170 (m br), 3094 (w br), 2924 (m br), 2857 (w sh), 2694 (w br), 1596 (m), 1558 (w sh), 1529 (vs), 1466 (m), 1418 (m), 1369 (s), 1326 (m), 1258 (s), 1215 (vs), 1200 (s sh), 1143 (s), 1116 (m), 1052 (s), 1015 (m), 995 (m), 871 (w), 835 (m), 783 (w), 751 (s), 736 (w), 712 (vw), 701 (vw), 696 (vw), 668 (vw), 638 (w), 591 (m), 453 (w).

Scheme 1. Synthesis of 5-(Trinitromethyl)-2H-tetrazole 4

**Synthesis of Hydrazinium 5-(Dinitromethyl)tetrazolate (12).**

A solution of hydrazine (2.00 g, 62.5 mmol) in water (5 mL) was slowly added to a solution of 5-(trinitromethyl)-2H-tetrazole (0.438 g, 2.00 mmol) in water (5 mL). After gas evolution ceased, the obtained yellow solution was taken to dryness by a stream of nitrogen. Hydrazinium 5-(dinitromethyl)tetrazolate (12) was obtained as dark yellow crystals (0.437 g). Theoretical mass expected for 2.00 mmol of  $C_2H_{10}N_{10}O_4 = 0.476$  g (yield = 91.7%). DTA ( $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ )  $152.2\text{ }^\circ\text{C}$  explosion. Recrystallization from water resulted in isolation of hydrazinium 5-(dinitromethyl)tetrazolate monohydrate ( $12\cdot H_2O$ ,  $C_2H_{10}N_{10}O_4\cdot H_2O$ ) as yellow crystals. DTA ( $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ )  $151.0\text{ }^\circ\text{C}$  explosion.  $^1\text{H}$  NMR ( $D_2O$ , ppm)  $\delta$  1.2 and 1.9 br ( $N_2H_5$ ).  $^{13}\text{C}$  NMR ( $D_2O$ , ppm)  $\delta$  129.0 br s [ $C(NO_2)_2$ ]; 156.4 s ( $CN_4$ ).  $^{14}\text{N}$  NMR ( $D_2O$ , ppm)  $\delta$  -24.6,  $\tau_{1/2} = 90$  Hz ( $NO_2$ );  $\delta$  -70,  $\tau_{1/2} = 680$  Hz ( $CN_4$ ); -332 ppm,  $\tau_{1/2} = 390$  Hz ( $N_2H_5$ ). Raman (1064 nm, 40 mW)  $\nu$  ( $\text{cm}^{-1}$ ) = 3352 (0.3), 3342 (0.2), 3293 (0.7), 3265 (0.3), 3255 (0.3), 3220 (0.5), 3150 (0.6), 1648 (0.4), 1625 (0.3), 1588 (0.4), 1523 (2.3), 1501 (1.2 sh), 1487 (0.9), 1467 (0.4), 1431 (1.8), 1406 (1.1), 1363 (7.2), 1268 (0.4), 1214 (3.0), 1202 (2.0 sh), 1148 (1.6), 1132 (2.7), 1103 (1.1), 1079 (1.8), 1072 (1.2 sh), 1023 (8.7), 945 (1.2), 823 (10.0), 789 (0.5), 756 (0.6), 735 (0.7), 482 (2.3), 448 (1.6), 422 (2.0), 604 (0.3), 369 (0.4), 315 (0.5), 267 (1.1), 168 (3.5), 145 (5.1). IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) = 3500–3380 (s), 3350–3250 (s), 3230–2900 (s), 2694 (vw br), 2618 (w br), 1615 (m br), 1528 (s), 1505 (vw), 1446 (m sh), 1430 (s), 1383 (m), 1356 (m), 1270 (m sh), 1230 (vs), 1219 (vs), 1130 (vs), 1083 (m br), 1013 (s), 957 (m br), 826 (m), 789 (vw), 750 (m), 736 (nw), 637 (w), 593 (w), 490 (nw), 449 (w).

**Synthesis of 5-(Dinitromethylene)-4,5-dihydro-1H-tetrazole (13).**

Hydrazinium 5-(dinitromethyl)tetrazolate (0.238 g, 1.00 mmol) or hydroxylammonium 5-(dinitromethyl)tetrazolate (0.207 g, 1.00 mmol) was dissolved in 2 M sulfuric acid (10 mL) and the solution was extracted three times with ethyl acetate (5 mL each). The combined organic phases were dried over magnesium sulfate, and the solvent was evaporated on a rotary evaporator. 5-(Dinitromethylene)-4,5-dihydro-1H-tetrazole (13) was obtained as white solid (0.150 g). Theoretical mass expected for 1.00 mmol of  $C_2H_2N_6O_4 = 0.174$  g (yield = 85.9%). DTA ( $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ )  $92.2\text{ }^\circ\text{C}$  explosion. Recrystallization from acetone/water resulted in isolation of 5-(dinitromethylene)-4,5-dihydro-1H-tetrazole dihydrate ( $C_2H_2N_6O_4\cdot 2H_2O$ ,  $13\cdot 2H_2O$ ) as colorless crystals. DTA ( $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ )  $103.1\text{ }^\circ\text{C}$  explosion.  $^1\text{H}$  NMR ( $DMSO-d_6$ , ppm)  $\delta$  11.0 br (NH).  $^{13}\text{C}$  NMR ( $DMSO-d_6$ , ppm)  $\delta$  122.0 [ $C(NO_2)_2$ ]; 150.4 ( $CN_4$ ).  $^{14}\text{N}$  NMR ( $DMSO-d_6$ , ppm)  $\delta$  -24.1,  $\tau_{1/2} = 80$  Hz ( $NO_2$ );  $\delta$  -42/-64,  $\tau_{1/2} = 550/600$  Hz ( $CN_4$ ). Raman (488 nm, 100 mW)  $\nu$  ( $\text{cm}^{-1}$ ) = 3058 (0.4), 2958 (0.5), 1581 (6.4), 1523 (0.4), 1509 (0.4), 1493 (0.4), 1460 (0.2), 1419 (6.3), 1396 (1.0), 1314 (10.0), 1290 (2.5), 1278 (0.6 sh), 1242 (2.8), 1194 (1.0), 995 (8.3), 841 (5.6), 789 (3.3), 531 (1.6 broad), 492 (1.4 broad), 436 (3.1), 382 (0.7), 374 (0.7), 357 (0.7), 300 (1.6), 274 (0.5), 250 (0.4), 230 (1.0). IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) = 3400–3000 (m br), 1585 (s), 1524 (vs), 1479 (m), 1421 (m), 1362 (m), 1353 (m), 1330 (m), 1318 (w sh), 1248 (s), 1226 (w sh), 1201 (vs), 1183 (w sh), 1144 (m), 1114

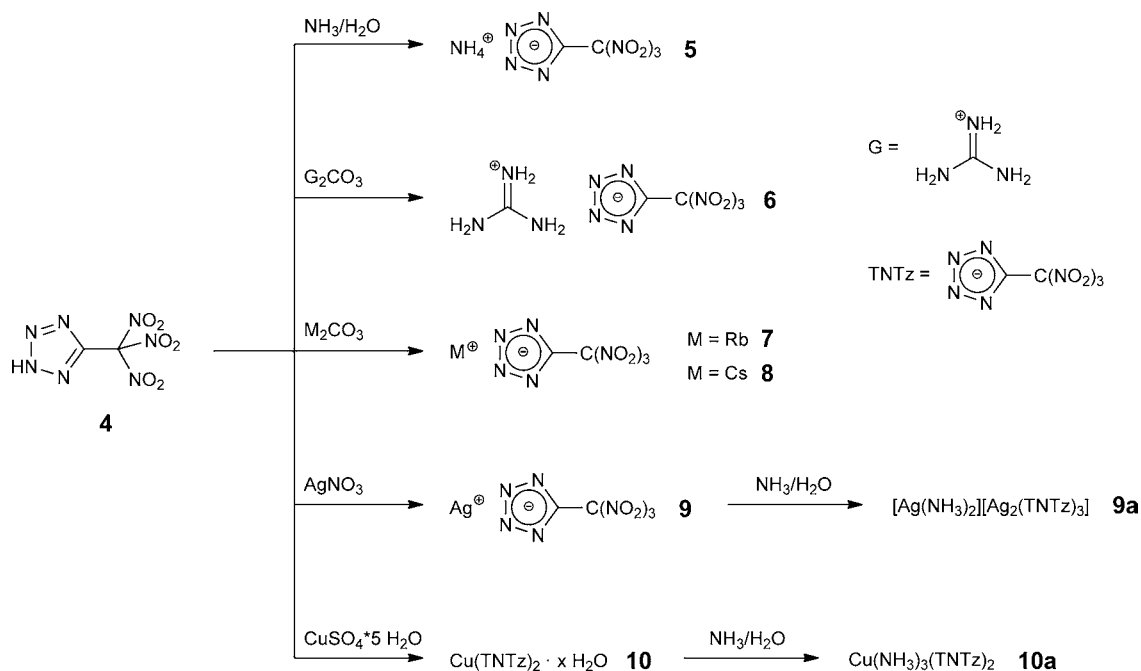
(m), 1072 (w sh), 1054 (s), 1020 (m), 998 (m), 837 (m), 800 (w), 753 (s), 744 (w sh), 712 (w sh), 429 (m).

**Synthesis of Potassium 5-(Dinitromethylene)-1H-tetrazolate (14).**

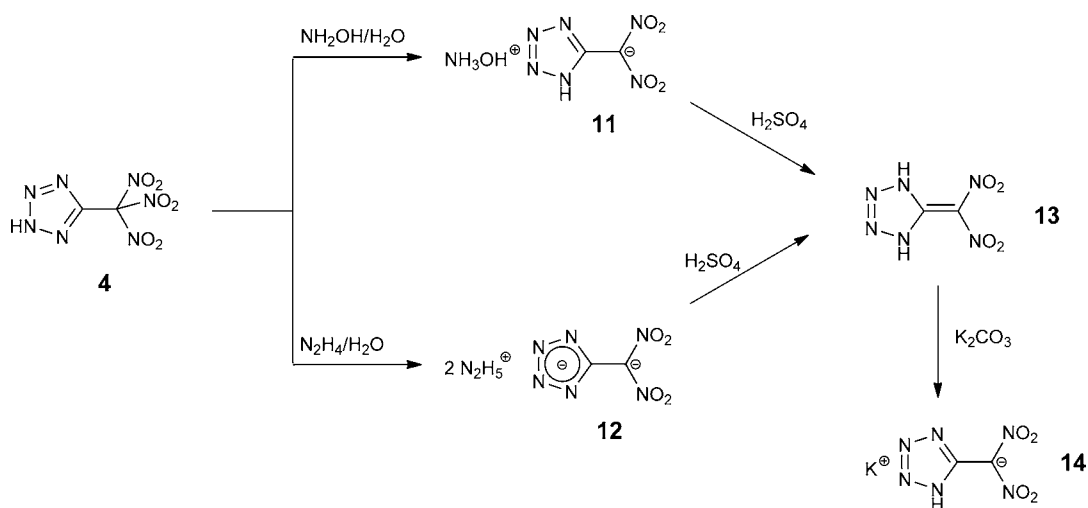
A solution of 5-(dinitromethylene)-4,5-dihydro-1H-tetrazole (0.174 g, 1.00 mmol) in acetone (5 mL) was added to a stirred suspension of potassium carbonate (0.138 g, 1.00 mmol) and acetone (5 mL). After 30 min, the reaction mixture was filtered through a Buchner funnel and the filtrate was taken to dryness by a stream of nitrogen. Potassium 5-(dinitromethylene)-1H-tetrazolate (14) was obtained as pale yellow crystals (0.195 g). Theoretical mass expected for 1.00 mmol of  $C_2HKN_6O_4 = 0.212$  g (yield = 91.9%). DTA ( $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ )  $155.2\text{ }^\circ\text{C}$  explosion.  $^{13}\text{C}$  NMR ( $DMSO-d_6$ , ppm)  $\delta$  121.5 s [ $C(NO_2)_2$ ]; 149.4 s ( $CN_4$ ).  $^{14}\text{N}$  NMR ( $DMSO-d_6$ , ppm)  $\delta$  -24.5,  $\tau_{1/2} = 60$  Hz ( $NO_2$ );  $\delta$  -275,  $\tau_{1/2} = 200$  Hz (NH). Raman (1064 nm, 15 mW)  $\nu$  ( $\text{cm}^{-1}$ ) = 3240 (0.3 br), 1541 (2.0 sh), 1523 (10.0), 1487 (1.7), 1419 (1.0), 1397 (0.5), 1365 (9.1), 1336 (2.0), 1320 (5.0), 1246 (3.3), 1184 (7.3), 1147 (3.0), 1133 (2.1 sh), 1117 (2.0), 1052 (1.5), 1016 (1.1), 1001 (8.8), 840 (6.4), 780 (1.4), 473 (2.0), 453 (0.9), 440 (1.0 sh), 432 (1.4), 388 (0.7), 352 (1.2), 316 (0.5), 236 (0.7), 206 (0.3), 155 (3.1). IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) = 3217 (m br), 1616 (w br), 1539 (m sh), 1525 (m), 1478 (m), 1468 (w sh), 1419 (m), 1362 (m), 1334 (w), 1317 (m), 1244 (s), 1190 (w sh), 1182 (vs), 1142 (m), 1136 (w sh), 1113 (s), 1052 (vs), 1013 (w), 998 (m), 837 (m), 801 (m), 776 (w), 753 (m), 697 (m), 604 (w).

**X-ray Crystal Structure Determination.** Single-crystal X-ray diffraction data were collected on a Bruker Smart Apex Duo 3-circle platform diffractometer, equipped with an Apex II charge-coupled device (CCD) detector with the  $\chi$ -axis fixed at  $54.74^\circ$  and using Mo  $K\alpha$  radiation (Triumph curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryostream 700 apparatus for low-temperature data collection. A complete hemisphere of data was scanned on  $\omega$  ( $0.5^\circ$ ) with a run time of 1, 2, or 10 s/frame at a detector resolution of  $512 \times 512$  pixels by use of the BIS software package.<sup>18</sup> The frames were then integrated with the SAINT algorithm<sup>26</sup> to give the hkl files corrected for Lp/decay. Absorption correction was performed with the SADABS program.<sup>27</sup> The structures were solved by the direct method and refined on  $F^2$  by use of the Bruker SHELXTL software package.<sup>28–31</sup> All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared with the ORTEP-III for Windows V2.02 program.<sup>32</sup> Further crystallographic details for compounds 1 and 2 can be obtained from the Cambridge Crystallographic Data Centre [CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk] on quoting the deposition numbers CCDC 895075 and 895076) and for compounds 4–14 from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax (+49) 7247-808-666, e-mail crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request\_for\_deposited\_data.html] on quoting the deposition numbers CSD 425032–425043.

Scheme 2. Synthesis of 5-(Trinitromethyl)tetrazolate Salts 5–10a



Scheme 3. Synthesis of Dinitromethyltetrazoles 11–14



## RESULTS AND DISCUSSION

**Syntheses.** The employed synthetic routes for the preparation of HTNTz **4** are shown in Scheme 1. Initially, **4** was prepared from cyanoacetamide according to a slightly modified literature method.<sup>21</sup> Nitration of cyanoacetamide with fuming nitric acid in 20% oleum under anhydrous conditions resulted in formation of trinitroacetone nitrile **3**. Because of its reported sensitivity and instability,<sup>25</sup> **3** was not isolated as a neat compound and was handled only in the form of solutions in tetrachloromethane. The 1,3-dipolar cycloaddition reaction of **3** with  $\text{HN}_3$ , followed by extraction with dichloromethane, resulted in isolation of HTNTz **4** in approximately 60% yield.

Due to the high moisture sensitivity of the nitration step, as well as the sensitivity and instability of trinitroacetone nitrile **3**,<sup>25</sup> the following more convenient synthesis of HTNTz **4** was developed. The 1,3-dipolar cycloaddition of ethyl cyanoacetate with  $\text{HN}_3$ , followed by basic hydrolysis of the obtained ethyl

ester **1**, resulted in isolation of 1*H*-tetrazole-5-acetic acid **2**.<sup>23,24,33</sup> Nitration of **2** with fuming nitric acid in concentrated sulfuric acid, followed by extraction with dichloromethane, resulted in isolation of HTNTz **4** in 60% yield. In contrast to the fact that **4** was previously described as an orange-yellow oil,<sup>20</sup> it was obtained as colorless crystals that tend to explode upon impact, shock, and friction. The compound explodes upon heating at about 95 °C and is soluble in water, acetonitrile, dichloromethane, and acetone. HTNTz **4** is strongly acidic and reacts with bases yielding the formation of salts containing the 5-(trinitromethyl)tetrazolate ( $\text{TNTz}^-$ ) anion (Scheme 2).

Ammonium 5-(trinitromethyl)tetrazolate **5** was obtained in quantitative yield by a convenient acid–base reaction between aqueous solutions of **4** and ammonia. The guanidinium, rubidium, and cesium salts **6–8** were obtained in quantitative yields by reaction of a solution of **4** in acetone with an excess of the corresponding carbonate. Silver and copper(II) 5-

**Table 1. Crystallographic Data and Structure Determination Details for Tetrazoles 1, 2, and 4**

	1	2	4
formula	C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>2</sub> HN <sub>7</sub> O <sub>6</sub>
weight (g/mol)	156.12	128.10	219.10
temp (K)	100(2)	100(2)	100(2)
crystal system	orthorhombic	monoclinic	monoclinic
space group	<i>Pca</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	9.7840(3)	7.2196(11)	5.9141(3)
<i>b</i> (Å)	11.0429(4)	7.3128(10)	21.5244(11)
<i>c</i> (Å)	6.5982(2)	10.0239(14)	6.0357(3)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	90	102.734(3)	99.0760(10)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	712.89(4)	516.20(13)	758.71(7)
<i>Z</i>	4	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.455	1.648	1.918
$\mu$ (mm <sup>-1</sup> )	0.116	0.140	0.188
<i>F</i> (000)	328	264	440
reflns collected	16 196	12 286	18 128
ind reflns	2149	1578	2313
<i>R</i> <sub>int</sub>	0.0260	0.0364	0.0399
no. of params	105	85	136
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0255	0.0339	0.0318
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0669	0.0841	0.0725
GoF	1.073	1.043	1.012

(trinitromethyl)tetrazolate **9** and **10** were obtained as colorless or blue amorphous precipitates when aqueous solutions of silver nitrate or copper(II) sulfate, respectively, were added to aqueous solutions of **4** (Scheme 2). Colorless or intense blue crystals of the ammonia adducts **9a** and **10a**, respectively, were obtained by recrystallization of the amorphous precipitates **9** and **10** from aqueous ammonia solutions. While all 5-(trinitromethyl)tetrazolates of this work are energetic and can explode upon provocation (heat or mechanical shock), compounds **7–10** are especially sensitive and treacherous. For example, in several instances, crystals of **7** and **8** exploded during crystallization without any further provocation. These salts should be handled with great care, proper safety precautions and only on a small scale.

While the conversion of trinitromethyl-substituted imidazoles and triazoles into the corresponding dinitromethylide salts by use of hydroxylamine has previously been reported,<sup>14,17,34</sup> the mechanism of these reactions is unknown. In an analogous conversion, yellow to orange hydroxylammo-

nium 5-(dinitromethyl)-1*H*-tetrazolate **11** was obtained in over 90% isolated yield when neat HTNTz **4** or an aqueous solution of **4** was reacted with 50% aqueous hydroxylamine (Scheme 3). Exposure of neat HTNTz **4** to 100% hydrazine resulted in a violent reaction with ignition of the material followed by an explosion. However, when an aqueous solution of **4** was reacted with 50% aqueous hydrazine, yellow to orange hydrazinium 5-(dinitromethyl)tetrazolate **12** was obtained in high yield (scheme 3). Recrystallization of **12** from water resulted in crystals of the monohydrate **12**·H<sub>2</sub>O as pale orange crystals. Treatment of **11** and **12** with 2 M sulfuric acid resulted in formation of colorless 5-(dinitromethylene)-4,5-dihydro-1*H*-tetrazole **13** in good yields of 85%. The compound was recrystallized from acetone/water and isolated as the crystalline dihydrate **13**·2H<sub>2</sub>O. Treatment of **13** or **13**·2H<sub>2</sub>O with potassium carbonate in acetone solution resulted in formation of potassium 5-(dinitromethyl)-1*H*-tetrazolate **14**, which was isolated as pale yellow crystals in over 90% yield.

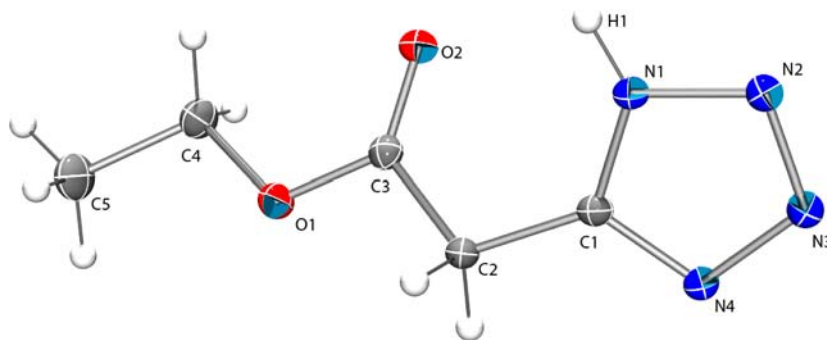
**X-ray Crystal Structures.** Single crystals suitable for X-ray crystal structure determination were obtained for compounds **1**, **2**, **4–8**, **9a**, **10a**, and **11–14**. The relevant data and parameters for the X-ray measurements and refinements of the tetrazoles **1**, **2**, and **4** are summarized in Table 1. For all three compounds, the hydrogen atom of the tetrazole ring has been located via the difference electron density map.

The molecular structure of the ethyl ester **1** is shown in Figure 1, and the geometric parameters of the CN<sub>4</sub> ring are summarized in Table 2. The observed bond length pattern within the five-membered ring [N2–N3 1.296(1) Å, C1–N4 1.328(1) Å, C1–N1 1.338(1) Å, N1–N2 1.352(1) Å, and N3–N4 1.368(1) Å] indicates significant double-bond character for bonds N2–N3 and C1–N4. This conclusion is further supported by the fact that the hydrogen atom of the tetrazole ring is located solely at N1 and is in good agreement with the common description of such compounds in the literature.<sup>24</sup>

The corresponding free acid **2** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*. Table 2 summarizes selected bond lengths and angles of **2**, and Figure 2 depicts the molecular structure of the compound. The observed bond lengths pattern of the five-membered ring is very similar to that of compound **1**.

The molecular structure of 5-(trinitromethyl)-2*H*-tetrazole is depicted in Figure 3, while Table 2 summarizes the bond lengths and angles of the tetrazole ring in this compound. The crystal packing of the compound is dominated by hydrogen bonding (Supporting Information).

In comparison to compounds **1** and **2**, the geometry of the five-membered ring in **4** is different. While the hydrogen atom



**Figure 1.** X-ray crystal structure of **1**. Hydrogen atoms are shown as spheres of arbitrary radius. Thermal displacement ellipsoids are set at 50% probability.

Table 2. Selected Bond Lengths and Angles for Compounds 1, 2, and 4–14<sup>a</sup>

	1		2		4		5		6		7		8		9a		10a		11		12		12·H <sub>2</sub> O		13·2H <sub>2</sub> O		14				
C1–N1	1.3375(10)	1.3392(13)	1.3242(14)	1.3362(13)	1.3334(14)	1.3351(14)	1.3373(16)	1.323(7)	1.326(3)	1.3560(11)	1.3344(12)	1.3382(10)	1.3407(11)	1.3462(17)																	
C1–N4	1.3276(10)	1.3290(13)	1.3519(14)	1.3349(13)	1.3383(15)	1.3352(14)	1.3341(16)	1.334(6)	1.333(3)	1.3378(12)	1.3391(11)	1.3412(10)	1.3407(11)	1.3466(17)																	
N1–N2	1.3516(9)	1.3444(13)	1.3226(13)	1.3392(12)	1.3390(14)	1.3441(13)	1.3392(16)	1.335(5)	1.347(3)	1.3451(11)	1.3423(11)	1.3433(10)	1.3534(10)	1.3490(16)																	
N2–N3	1.2958(10)	1.2951(13)	1.3213(13)	1.3241(12)	1.3256(15)	1.3249(14)	1.3273(16)	1.316(6)	1.318(3)	1.2920(11)	1.3181(11)	1.3180(10)	1.2790(16)	1.2971(17)																	
N3–N4	1.3681(9)	1.3638(13)	1.3202(13)	1.3380(12)	1.3393(14)	1.3451(13)	1.3418(16)	1.344(6)	1.342(3)	1.3592(11)	1.3467(11)	1.3453(10)	1.3534(10)	1.3550(16)																	
C1–C2	1.4858(10)	1.4888(15)	1.4912(15)	1.4827(13)	1.4766(16)	1.4782(15)	1.4778(18)	1.487(7)	1.477(3)	1.4534(12)	1.4622(12)	1.4643(11)	1.4320(17)	1.4491(19)																	
C2–N5	-	-	1.5391(14)	1.5358(13)	1.5258(15)	1.5302(14)	1.5315(16)	1.554(7)	1.541(3)	1.3823(12)	1.3846(11)	1.3859(10)	1.4029(10)	1.4013(17)																	
C2–N6	-	-	1.5309(14)	1.5315(18)	1.5431(15)	1.5383(14)	1.5372(17)	1.529(7)	1.518(3)	1.4216(12)	1.3873(11)	1.3841(10)	1.4029(10)	1.4118(17)																	
C2–N7	-	-	1.5451(14)	1.5448(13)	1.5408(15)	1.5491(14)	1.5487(17)	1.527(7)	1.539(3)	-	-	-	-	-																	
C1–N1–N2	108.89(7)	109.57(9)	100.77(9)	103.49(8)	103.45(10)	103.44(9)	103.43(11)	103.2(4)	102.5(2)	109.04(8)	105.04(8)	104.98(7)	110.11(8)	109.45(11)																	
C1–N4–N3	106.25(7)	105.76(9)	105.42(9)	103.69(8)	103.33(9)	103.28(9)	103.23(10)	103.5(4)	103.6(2)	106.15(8)	104.98(7)	104.54(7)	110.11(8)	105.79(11)																	
N1–N2–N3	106.68(6)	105.88(9)	114.76(9)	109.87(8)	109.86(10)	109.70(9)	109.68(11)	110.7(4)	110.8(2)	106.55(7)	109.57(8)	109.28(7)	107.92(5)	105.99(11)																	
N2–N3–N4	110.19(6)	111.11(9)	105.77(9)	109.70(8)	109.82(10)	109.88(9)	109.96(11)	108.9(4)	108.9(2)	111.19(8)	109.08(7)	109.69(7)	107.92(5)	111.58(12)																	
N1–C1–N4	107.99(7)	107.68(9)	113.27(9)	113.24(9)	113.53(10)	113.68(9)	113.69(11)	113.7(4)	114.1(2)	107.08(8)	111.34(8)	111.51(7)	103.93(10)	107.19(11)																	
N1–C1–C2	127.09(7)	127.70(9)	122.95(10)	122.48(9)	122.30(10)	118.97(9)	119.45(11)	122.5(4)	124.7(2)	125.18(8)	123.12(8)	124.08(7)	128.03(5)	125.39(11)																	
C1–C2–N5	-	-	113.33(9)	113.45(8)	111.14(9)	114.93(9)	115.22(10)	111.5(4)	110.2(2)	119.90(8)	118.30(8)	118.82(7)	119.89(5)	119.99(11)																	
N5–C2–N6	-	-	108.05(8)	109.79(8)	107.51(9)	108.93(8)	108.46(10)	107.3(4)	107.4(2)	119.96(8)	121.90(8)	121.49(7)	120.21(11)	118.98(11)																	

<sup>a</sup>Bond lengths are given in angstroms; bond angles are given in degrees.

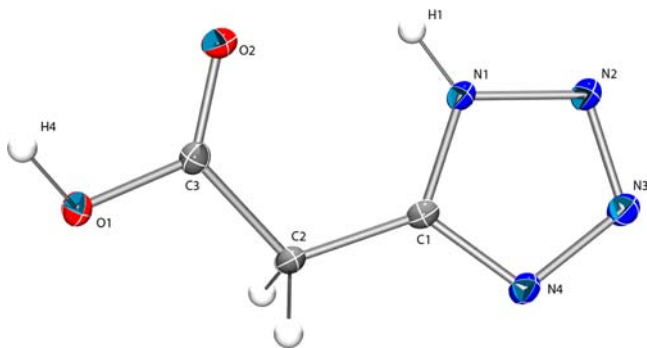


Figure 2. Molecular unit of 2 in the crystal. Hydrogen atoms are shown as spheres of arbitrary radius. Thermal displacement ellipsoids are set at 50% probability.

of the tetrazole moiety in compounds 1 and 2 is located at the 1-position of the ring (N1), in HTNTz the hydrogen atom is solely located at the 2-position (N2) of the five-membered ring. The different location of the hydrogen atom can be attributed to the much stronger electron-withdrawing effect of the trinitromethyl group in comparison to the CH<sub>2</sub>COOR group. The different location of the tetrazole hydrogen atom affects the bond lengths pattern within the five-membered ring. While the distance C1–N1 is longer than the one for C1–N4 in compounds 1 and 2, it is the opposite for compound 4. In HTNTz, the distance between C1 and N1 [1.324(1) Å] is 0.02 Å shorter than that between C1 and N4. While the N–N distances in the five-membered rings of 1 and 2 differ by about 0.06 Å, in 4 these distances can be considered identical within their margins of error.

The solid-state structure of ammonium 5-(trinitromethyl)-2H-tetrazolate 5 consists of ammonium cations and 5-

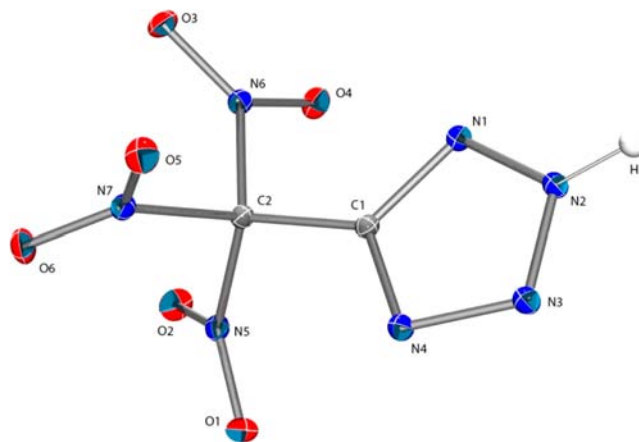
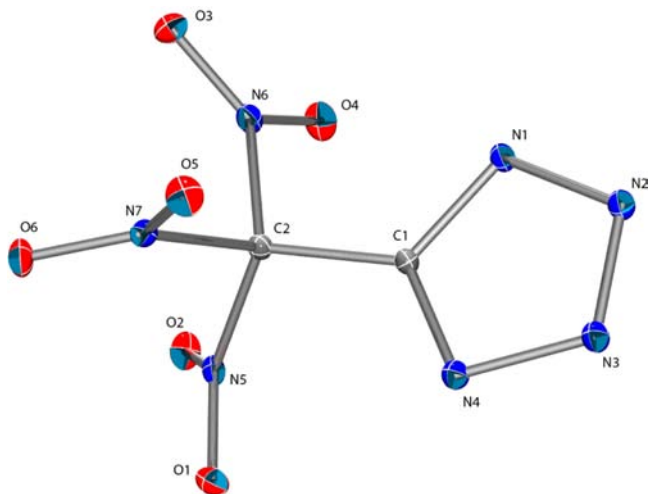


Figure 3. Molecular structure of 5-(trinitromethyl)-2H-tetrazolate 4 in the crystal. The hydrogen atom is shown as a sphere of arbitrary radius. Thermal displacement ellipsoids are set at 30% probability.

(trinitromethyl)-2H-tetrazolate (TNTz<sup>-</sup>) anions that are associated through hydrogen bonds (Supporting Information). Figure 4 shows the structure of the 5-(trinitromethyl)-tetrazolate anion in this salt, and further crystallographic details of the structure are listed in Table 3. The observed bond lengths and angles for the TNTz<sup>-</sup> anion are summarized in Table 2.

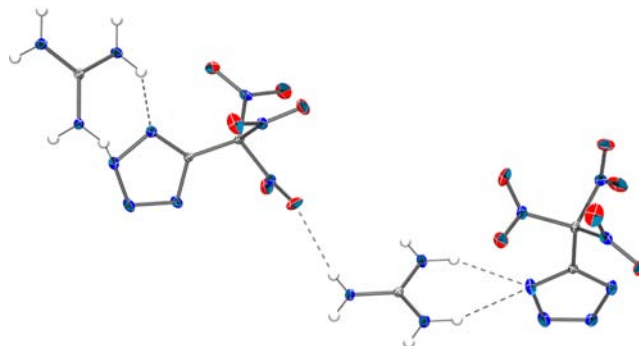
Guanidinium 5-(trinitromethyl)-2H-tetrazolate 6 crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* (*Z* = 8). The observed bond lengths and angles for the 5-(trinitromethyl)tetrazolate anion in the guanidinium salt 6 are very similar to those previously discussed for compound 5 and are summarized in Table 2, while further details of the structure determination and crystallographic parameters are listed in Table 3. As has already



**Figure 4.** Structure of the 5-(trinitromethyl)-2*H*-tetrazolate anion in compound **5**. Thermal displacement ellipsoids are drawn at 30% probability.

been observed for the ammonium salt **5**, the solid state packing in **6** is defined by strong hydrogen bonding between the guanidinium cations and the anions (Figure 5).

The observed crystal structures of the rubidium salt **7** and cesium salt **8** of the 5-(trinitromethyl)-2*H*-tetrazolate anion are isostructural. Both compounds crystallize in the triclinic space group *P*-1 with two formula units in the unit cell. As can be seen from Table 3, even the unit cell parameters are very similar, with the cesium salt having a slightly larger unit cell volume of 453.85(2) Å<sup>3</sup> compared to 423.78(2) Å<sup>3</sup> for the Rb salt. The basic geometry of the anion in both compounds is identical to that observed for the NH<sub>4</sub><sup>+</sup> salt **5**, which is depicted in Figure 4. Selected bond lengths and angles for the TNTz<sup>-</sup> anion in compounds **7** and **8** are listed in Table 2. The solid-



**Figure 5.** Asymmetric unit in the crystal structure of guanidinium salt **6** with hydrogen bonding. For clarity, only some of the observed hydrogen bonds are included. Hydrogen atoms are shown as spheres of arbitrary radius.

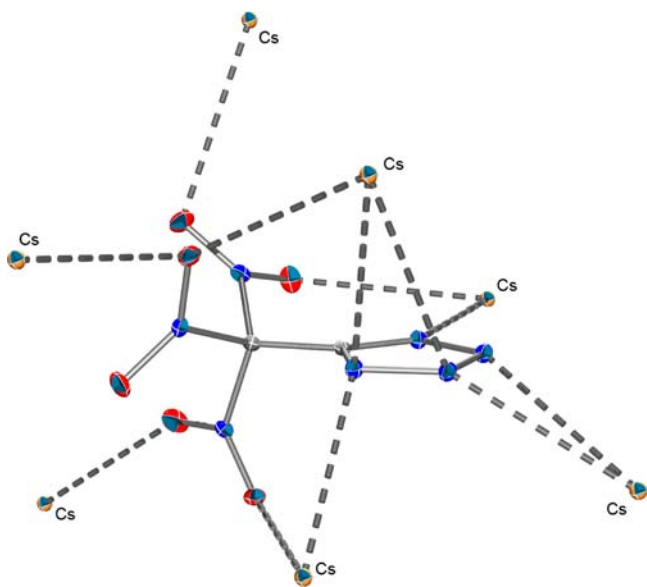
state structures of the Rb and Cs salts do not consist of isolated ions but are dominated by strong interactions between the metal cation and the nitrogen atoms of the tetrazolate ring and also six oxygen atoms from the nitro groups of the anion (Figure 6). The closest Rb–N and Cs–N distances are 2.951(1) and 3.119(1) Å (M–N4), respectively, and the closest Rb–O and Cs–O distances are 3.0312(9) and 3.159(1) Å (M–O6), respectively.

All attempts to grow single crystals of AgTNTz **9** suitable for X-ray structure determination were unsuccessful. Recrystallization of an amorphous sample of **9** from an aqueous ammonia solution resulted in crystals of the ammonia adduct ([Ag(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Ag<sub>2</sub>(TNTz)<sub>3</sub>]<sub>2</sub>)<sub>2</sub> **9a** instead. Selected crystallographic data of compound **9a** are listed in Table 3. The crystal structure of **9a** contains isolated [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations and polymeric anion chains. The anion chains are made up from [Ag<sub>2</sub>(TNTz)<sub>3</sub>]<sup>-</sup> units in which two silver atoms are linked in a 1,2-fashion by three bridging TNTz<sup>-</sup> anions. The resulting

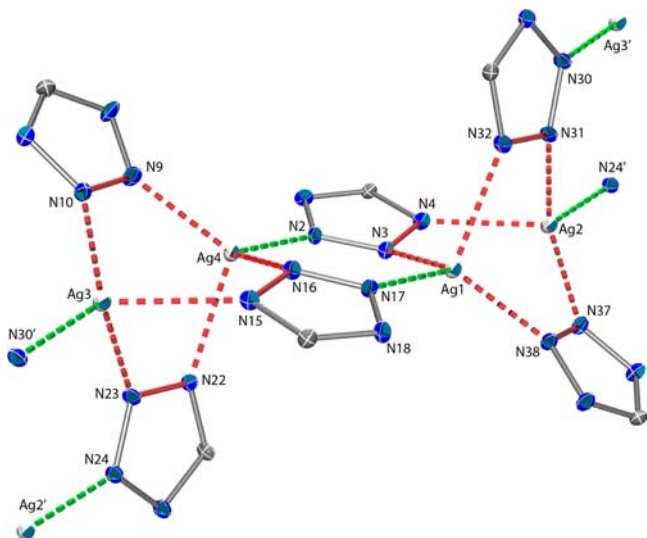
**Table 3.** Crystallographic Data and Structure Determination Details for Trinitromethyl-2*H*-tetrazolates **5**–**10a**

	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9a</b>	<b>10a</b>
formula	C <sub>2</sub> H <sub>4</sub> N <sub>8</sub> O <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>10</sub> O <sub>6</sub>	C <sub>2</sub> N <sub>7</sub> O <sub>6</sub> Rb	C <sub>2</sub> CsN <sub>7</sub> O <sub>6</sub>	C <sub>12</sub> H <sub>12</sub> Ag <sub>6</sub> N <sub>46</sub> O <sub>36</sub>	C <sub>4</sub> H <sub>9</sub> CuN <sub>17</sub> O <sub>12</sub>
weight (g/mol)	236.13	278.18	303.56	351.00	2023.90	550.82
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	7.0369(3)	9.8509(5)	5.8577(1)	5.9537(2)	11.7121(9)	7.6843(2)
<i>b</i> (Å)	7.3590(3)	8.8922(4)	7.5152(2)	7.7298(2)	22.171(4)	12.1514(3)
<i>c</i> (Å)	9.1760(4)	24.3416(12)	9.8610(2)	10.0994(3)	21.479(3)	19.8358(4)
$\alpha$ (deg)	104.8260(10)	90	85.1310(10)	84.2842(5)	90	90
$\beta$ (deg)	91.8040(10)	100.636(1)	78.4680(1)	79.0115(5)	91.600(2)	90
$\gamma$ (deg)	109.1510(10)	90	88.4250(10)	88.5204(5)	90	90
<i>V</i> (Å <sup>3</sup> )	430.45(3)	2095.60(18)	423.78(2)	453.85(2)	5575.3(15)	1852.17(8)
<i>Z</i>	2	8	2	2	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.822	1.763	2.379	2.568	2.411	1.975
$\mu$ (mm <sup>-1</sup> )	0.175	0.164	5.878	4.114	2.208	1.286
<i>F</i> (000)	240	1136	292	328	3904	1108
reflns collected	10 695	50 468	24 037	11 222	130 059	31 958
ind reflns	2585	6349	3719	2721	16 785	4222
<i>R</i> <sub>int</sub>	0.0262	0.0440	0.0316	0.0200	0.0701	0.0444
no. of params	159	353	145	146	908	311
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0318	0.0375	0.0203	0.018	0.0494	0.0310
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0777	0.0887	0.0406	0.0279	0.1223	0.0526
GoF	1.074	1.024	1.028	1.097	1.039	1.022

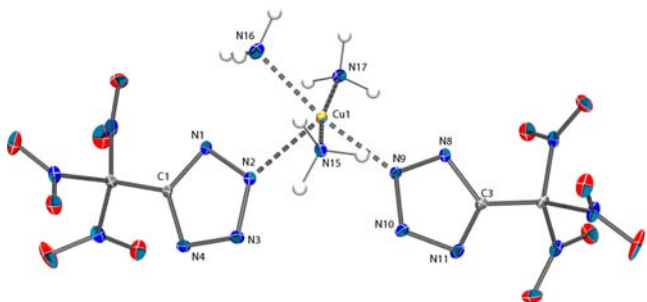




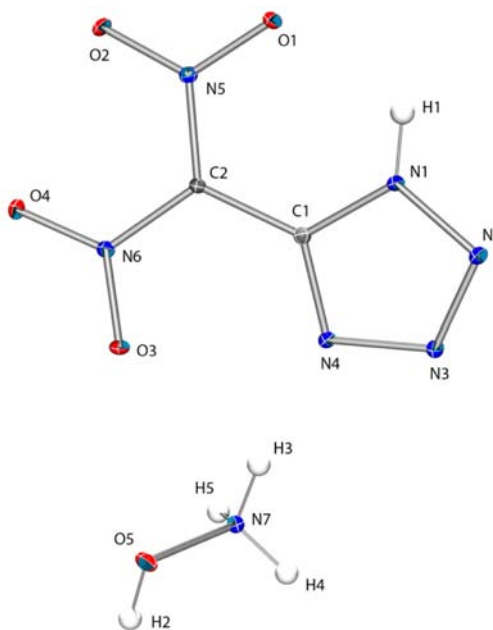
**Figure 6.** Interactions between cesium cation and 5-(trinitromethyl)-2*H*-tetrazolate anion in its cesium salt **8**.



**Figure 7.** Two  $[\text{Ag}_2(\text{TNTz})_3]^-$  units of an anion chain in the crystal structure of **9a**. The individual  $\text{Ag}_2(\text{TNTz})_3$  units are emphasized by red contacts, while contacts connecting the units are drawn in green. The trinitromethyl groups have been omitted for clarity.



**Figure 8.** Structure of  $\text{Cu}(\text{NH}_3)_3(\text{TNTz})_2$  **10a**. Hydrogen atoms have been omitted. Thermal displacement ellipsoids are drawn at the 30% probability level.



**Figure 9.** Molecular structure of hydroxylammonium 5-(dinitromethyl)-1*H*-tetrazolate **11**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

basic geometry is similar to the one of bicyclo[2.2.2]octane with the silver atoms acting as bridgeheads. The Ag–N distances within such units range from 2.267(4) to 2.478(5) Å. In addition, each of the Ag atoms is bonded to a nitrogen atom of a neighboring  $[\text{Ag}_2(\text{TNTz})_3]^-$  unit, resulting in the formation of an anion chain in which the  $[\text{Ag}_2(\text{TNTz})_3]^-$  units are interconnected through near-planar six-membered rings. Figure 7 shows two such interconnected  $[\text{Ag}_2(\text{TNTz})_3]^-$  units.

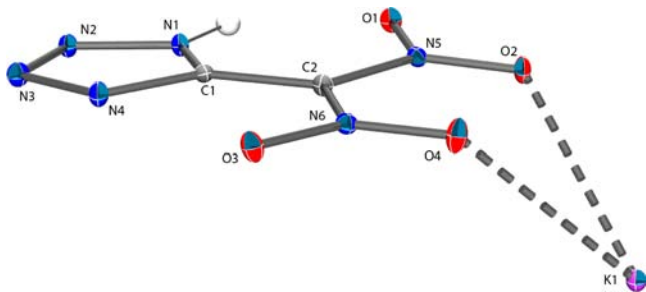
In analogy to the problems encountered in growing single crystals of **9**, all attempts to grow single crystals of the copper compound **10** suitable for X-ray diffraction were unsuccessful. Recrystallization of **10** from an aqueous ammonia solution resulted in intense blue crystals of  $\text{Cu}(\text{NH}_3)_3(\text{TNTz})_2$  **10a**.

The structure of the  $\text{Cu}(\text{NH}_3)_3(\text{TNTz})_2$  **10a** complex is depicted in Figure 8, and further crystallographic details for the crystal structure of **10a** are listed in Table 3. It can be seen from Figure 8 that the Cu atom is exclusively bound through the 2-position of the tetrazole ring. In accord with the  $d^9$  electron configuration of the central Cu atom, the ligand arrangement in the complex can be derived from a Jahn–Teller distorted octahedron in which one axial position remains unoccupied and the second axial position is occupied by one 5-(trinitromethyl)-2*H*-tetrazolate anion. The equatorial positions are occupied by three  $\text{NH}_3$  groups and one 5-(trinitromethyl)-2*H*-tetrazolate. The second axial position remains unoccupied. The equatorial Cu–N distances range from 2.006(2) to 2.029(2) Å. The longer axial Cu–N distance of 2.247(2) Å is in accordance with the Jahn–Teller distortion typically observed for  $d^9$  electron configuration.

The molecular structure of hydroxylammonium 5-(dinitromethyl)-1*H*-tetrazolate **11** is shown in Figure 9, and further crystallographic data are summarized in Table 4. Structural parameters of the 5-(dinitromethyl)-1*H*-tetrazolate anion in **11** are summarized in Table 2 and are in good agreement with the ones described previously for this compound.<sup>13,16</sup>

Table 4. Crystallographic Data and Structure Determination Details for Dinitromethyltetrazoles 11–14

	11	12	12·H <sub>2</sub> O	13·2H <sub>2</sub> O	14
formula	C <sub>2</sub> H <sub>5</sub> N <sub>7</sub> O <sub>5</sub>	C <sub>2</sub> H <sub>10</sub> N <sub>10</sub> O <sub>4</sub>	C <sub>2</sub> H <sub>12</sub> N <sub>10</sub> O <sub>5</sub>	C <sub>2</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	C <sub>2</sub> HKN <sub>6</sub> O <sub>4</sub>
weight (g/mol)	207.13	238.20	256.22	210.13	212.17
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>Pnma</i>	<i>P2<sub>1</sub></i>
<i>a</i> (Å)	9.1235(5)	9.9843(4)	11.3187(4)	10.605(3)	4.7849(2)
<i>b</i> (Å)	9.3899(5)	6.9914(3)	9.0679(3)	15.718(4)	9.1100(3)
<i>c</i> (Å)	8.1626(4)	13.8195(5)	10.1352(4)	4.8189(12)	7.5085(3)
$\alpha$ (deg)	90	90	90	90	90
$\beta$ (deg)	91.9210(10)	105.8260(10)	90.9770(10)	90	90.9830(10)
$\gamma$ (deg)	90	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	698.89(6)	928.09(6)	1040.09(6)	803.3(3)	327.25(2)
<i>Z</i>	4	4	4	4	2
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.969	1.705	1.636	1.738	2.153
$\mu$ (mm <sup>-1</sup> )	0.186	0.153	0.150	0.169	0.807
<i>F</i> (000)	424	496	536	432	212
reflins collected	7529	21 591	24 959	17 653	6491
ind reflins	2089	2813	3169	1212	1954
<i>R</i> <sub>int</sub>	0.0212	0.0317	0.0262	0.0408	0.0186
no. of params	131	185	202	73	122
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0300	0.0322	0.0289	0.0297	0.0201
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0806	0.0834	0.0796	0.0821	0.0527
GoF	1.043	1.040	1.060	1.098	1.058



**Figure 10.** Molecular structure of potassium 5-(dinitromethyl)-1*H*-tetrazolate **14**. Ellipsoids are drawn at the 30% probability level. The hydrogen atom is shown as a sphere of arbitrary radius. Selected distances and angles: K1–O2, 2.8318(10) Å; K1–O4, 2.7882(11) Å; O2–K1–O4, 52.87(3)°.

The dihydrazinium salt of 5-(dinitromethyl)tetrazole **12** crystallizes in the monoclinic space group *P2<sub>1</sub>/c* with four formula units in the unit cell. Recrystallization of **12** from water afforded crystals of the hydrate **12·H<sub>2</sub>O**, whose crystal structure has previously been described.<sup>13</sup> The obtained structures of the 5-(dinitromethyl)tetrazolate anion in **12** and **12·H<sub>2</sub>O** (see Supporting Information) are in good agreement with the one described previously for the sodium, ammonium, hydroxylammonium, and aminoguanidinium salts<sup>16</sup> and are summarized in Table 2.

Details of the obtained crystal structure of dinitromethylene-4,5-dihydro-1*H*-tetrazole dihydrate **13·2H<sub>2</sub>O** can be found in Table 4. The obtained structural parameters (Table 2) of the dinitromethylene-4,5-dihydro-1*H*-tetrazole molecule in **13·2H<sub>2</sub>O** are in good agreement with the ones described previously for this compound.<sup>16</sup>

The asymmetric unit in the crystal structure of potassium 5-(dinitromethyl)-1*H*-tetrazolate **14** is depicted in Figure 10. Crystallographic details of the structure are listed in Table 4.

**Stability of the Compounds.** The impact and friction sensitivities of the tetrazoles of this study were determined by use of a BAM fall hammer and BAM friction tester, respectively. The obtained sensitivities are summarized in Table 5, together with the oxygen balances (OB) of the compounds. 5-(Trinitromethyl)-2*H*-tetrazole **4** and the corresponding salts **7–9** as well as hydroxylammonium 5-(dinitromethyl)-1*H*-tetrazolate **11** are overoxidized and possess a positive oxygen balance; compounds **1, 2, 6, 10a**, and **12–14** are underoxidized with a negative oxygen balance; and ammonium 5-(trinitromethyl)tetrazolate **5** is oxygen-balanced. It is often assumed that a compound with an oxygen balance closer to zero will be more brisant, powerful, or sensitive. This relationship is not universally correct and there are many exceptions to this simple rule. For example, RbTNTz **7** and CsTNTz **8** have higher impact and friction sensitivities than NH<sub>4</sub>TNTz **5**, despite their more positive oxygen balances. However, the oxygen balance can be very useful in the processing of energetic materials formulations (e.g., rocket propellants or mixtures of explosives). In general, formulations with an oxygen balance close to zero yield higher performances than formulations that are over- or underoxidized.<sup>35</sup>

With the exception of ethyl 2-(1*H*-tetrazol-5-yl)acetate **1** and 1*H*-tetrazole-5-ethanoic acid **2**, all tetrazole compounds of this study proved to be highly energetic and sensitive to mechanical stress. While compounds **1** and **2** could not be exploded with impacts of up to 100 J, all studied nitro-2*H*-tetrazoles showed impact sensitivities of 30 J or less. The neutral 5-(nitromethyl)-2*H*-tetrazoles **4** and **13**, as well as the 5-(trinitromethyl)-2*H*-tetrazolates **5–8**, are highly sensitive and explode violently at impacts of under 5 J. By comparison of the sensitivity data of **9/9a**, **12/12·H<sub>2</sub>O**, and **13/13·2H<sub>2</sub>O**, it can be seen that incorporation of water or ammonia into the crystal lattice results in lowered impact sensitivity of the compound. The friction sensitivity of the compounds follows similar trends. Also, all compounds were screened for sensitivity toward

Table 5. Properties of Compounds 1, 2, and 4–14

compd	OB <sup>a</sup> (%)	T <sub>explosion</sub> (°C)	impact sensitivity <sup>b</sup> (J)	friction sensitivity <sup>c</sup> (N)
1	−123.0		>100	>360
2	−75.0		>100	>360
HTNTz, 4	+11.0	100.9	9.0	9.0
NH <sub>4</sub> TNTz, 5	0.0	115.7	6.0	20
GuaTNTz, <sup>d</sup> 6	−17.3	115.5	4.0	40
RbTNTz, 7	+7.9	119.6	0.5	<1
CsTNTz, 8	+6.8	129.9	0.5	<1
AgTNTz, 9	+7.4	123.4	5.0	5.0
([Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> [Ag <sub>2</sub> (TNTz) <sub>3</sub> ]) <sub>2</sub> , 9a	+12.3	122.8	9.5	5.0
Cu(TNTz) <sub>2</sub> ·xH <sub>2</sub> O, 10		122.8	2.0	80
Cu(NH <sub>3</sub> ) <sub>3</sub> (TNTz) <sub>2</sub> , 10a	−4.4	117.3	2.5	95
NH <sub>3</sub> OHDNTz, <sup>e</sup> 11	+3.4	149.9	5.5	144
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> DNTz, 12	−17.8	152.2	10.0	160
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> DNTz·H <sub>2</sub> O, 12·H <sub>2</sub> O	−16.7	151.0	30.0	>360
H <sub>2</sub> DNTz, 13	−9.9	92.2	5.0	64
H <sub>2</sub> DNTz·2H <sub>2</sub> O, 13·2H <sub>2</sub> O	−8.1	103.1	15.0	168
KHDNTz, 14	−8.0	155.2	3.5	10

<sup>a</sup>OB = oxygen balance. <sup>b</sup>The impact sensitivity of RDX was found as 7.0 J on the instrument used. <sup>c</sup>The friction sensitivity of RDX was found as 160 N on the instrument used. <sup>d</sup>Gua = guanidinium. <sup>e</sup>HDNTz = 5-dinitromethylene-4,5-dihydro-1H-tetrazole.

electrostatic discharge by exposing small amounts (~5 mg) to sparks from a Tesla coil (~20 kV). All compounds, except 4, failed to explode under these conditions.

The thermal stabilities of all compounds of this study were determined by differential thermal analysis (DTA) scans with a heating rate of 5 °C·min<sup>−1</sup>. The results of these scans are summarized in Table 5. As expected, compounds 1 and 2 did not explode but melted at onset temperatures of 124.4 °C (lit. 128–130 °C)<sup>24</sup> and 167.1 °C (lit. 170 °C),<sup>24</sup> respectively. All thermogravimetric scans of compounds 4–14 resulted in violent explosive decompositions at temperatures less than 160 °C. While the parent compound 5-(trinitromethyl)-2H-tetrazole 4 explodes at a temperature of about 100 °C, the corresponding salts with the 5-(trinitromethyl)-2H-tetrazolate anion explode at higher temperatures ranging from 115 to 130 °C. It is interesting to note that the nature of the cation has only a limited effect on the decomposition temperature of the salt. A comparison of the decomposition temperatures of compounds 9/9a, 10/10a, 12/12·H<sub>2</sub>O, and 13/13·2H<sub>2</sub>O indicates that the incorporation of water or ammonia in the crystal does not have a significant influence on the thermal stability of these materials. As already observed for HTNTz and its related compounds, the salts 11, 12, and 14 with the (dinitromethyl)tetrazolate anion have higher decomposition temperatures (150–155 °C) than the related free acid 13 and its dihydrate 13·2H<sub>2</sub>O, which decompose at 92.2 and 103.1 °C, respectively (lit. 88 °C).<sup>16</sup>

**Spectroscopy.** With the exception of compound 3, all compounds of this study have been characterized by their IR and Raman spectra. The observed frequencies and intensities are listed in the Experimental Section. In addition, compounds 1, 2, 4–8, and 11–14 were also characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N, and in some cases <sup>15</sup>N NMR spectroscopy. The recorded chemical shifts are also listed in the Experimental Section. The <sup>14</sup>N NMR spectra of the nitromethyltetrazoles are dominated by the NO<sub>2</sub> groups, which result in relatively sharp signals (τ<sub>1/2</sub> < 100 Hz) at around −25 to −35 ppm. The resonances of the nitrogen atoms of the tetrazole ring result in one broad feature (τ<sub>1/2</sub> ~700–1000 Hz) in the <sup>14</sup>N spectrum at about −45 to −65 ppm. Even in the <sup>15</sup>N NMR spectra, it was not possible to

resolve individual signals for the chemically nonequivalent nitrogen atoms of the tetrazole ring. The <sup>13</sup>C NMR resonance for the carbon atom of the tetrazole ring was observed in the range 145–160 ppm. The carbon resonance of the C(NO<sub>2</sub>)<sub>3</sub> and C(NO<sub>2</sub>)<sub>2</sub> groups at around 120–125 ppm was less intense, broader, and more difficult to observe than that of the CN<sub>4</sub> ring. In the case of the C(NO<sub>2</sub>)<sub>3</sub> group in 5-(trinitromethyl)-2H-tetrazole, it was possible to resolve the <sup>1</sup>J(<sup>13</sup>C<sup>14</sup>N) coupling (7.6 Hz), which resulted in a septet in the <sup>13</sup>C spectrum.

## CONCLUSION

A new and convenient synthesis of 5-(trinitromethyl)-2H-tetrazole based on the nitration of 1H-tetrazole-5-acetic acid was developed. This synthesis circumvents the handling of dangerously sensitive trinitroacetonitrile. For the first time, 5-(trinitromethyl)-2H-tetrazole was fully characterized, including an X-ray structure determination. The compound was converted into ammonium, guanidinium, rubidium, cesium, copper(II), and silver 5-(trinitromethyl)-2H-tetrazolates. The reactions of 5-(trinitromethyl)-2H-tetrazole with hydroxylamine or hydrazine give easy access to 5-(dinitromethyl)-tetrazoles. All compounds in this study have been fully characterized by their X-ray crystal structures, decomposition temperatures, and vibrational and multinuclear NMR spectra.

## ASSOCIATED CONTENT

### Supporting Information

Sixty-four figures and 102 tables with characterization of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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