



## Less Sensitive Transition Metal Salts of the 5-Nitrotetrazolate Anion

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**Abstract:** Transition metal (silver and copper) salts of the 5-nitrotetrazolate (NT) anion (**1** and **2**) have been synthesized and characterized by analytical and spectroscopic methods. Standard BAM tests revealed extremely high sensitivity values for these compounds. The combination with the ethylenediamine ligand in salts **3** and **4** decreases the sensitivities in comparison to salts **1** and **2** making for much less hazardous handling and rendering the synthesis of NT salts more accessible for up-scaling. Additionally, a copper ammonia adduct of the NT anion (**5**) was synthesized, which shows the particularity of being able to be initiated by a laser beam, thus, decreasing the risk of accidental initiation, which often accompanies the use of primary explosives.

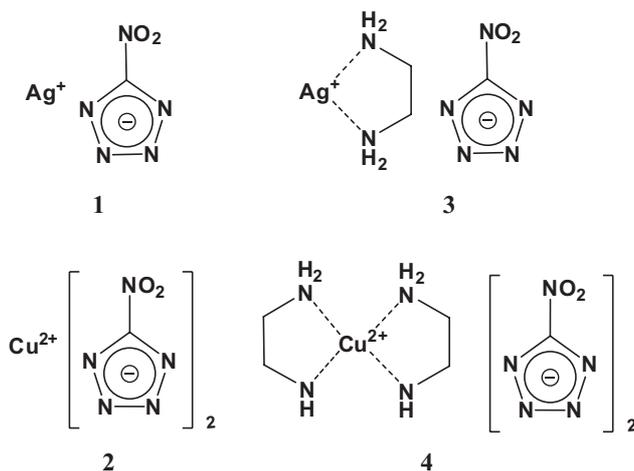
**Keywords:** transition metals (Ag, Cu), 5-nitrotetrazolate anion, primary explosives, initial safety testing

## Introduction

In the quest for new energetic materials [1] with high nitrogen and low carbon contents [2] several groups around the world are currently directing their efforts towards the investigation of HEDMs (High Energy Density Materials) based on tetrazoles [3]. This interest is due to the good compromise of properties that tetrazole-based energetic materials have. On one side, they combine high energies

(due to the high nitrogen content) and on the other, they possess surprisingly high thermal and kinetic stabilities (due to aromaticity). In addition, combination of a tetrazole moiety with energetic groups containing oxygen such as nitro groups ( $R-NO_2$ ), [4] nitrate esters ( $R-O-NO_2$ ) [5] or nitramines ( $R_2N-NO_2$ ) [6] is of utmost interest.

In the above context,  $Fe^{2+}$  and  $Co^{2+}$  complexes of the 5-nitrotetrazolate (NT) anion were investigated as potential replacements for lead-based primaries. [7, 8] Furthermore,  $Hg^+$ ,  $Hg^{2+}$  and  $Ag^+$  salts of NT [9] and several divalent transition metal salts (Fe, Co, Ni, Cu, Zn, Cr, Mn) of the same anion [10] were patented as primary explosives. However, the synthesis and handling of these highly sensitive materials is not always trouble-free and it has resulted in many unwanted accidents in the past. In addition, to metal-based NT salts, several heterocycle-based salts of the NT anion with prospective use as high-explosives and/or propellants have been investigated in the recent past [11]. Unfortunately, the preparation of such materials is often associated with the use of highly sensitive species with the corresponding associated hazards. In this paper, we would like to present the synthesis of two transition metal ( $Ag^+$  and  $Cu^{2+}$ ) complexes of the NT anion with ethylenediamine ligands (compounds **3** and **4**) as safer starting materials for the synthesis of energetic salts based on this anion and compare their energetic properties with those of the ligand-free compounds **1** and **2** (see Scheme 1). In addition, the synthesis of a new  $Cu^{2+}$  salt with the NT anion and ammonia ligands (**5**) is also presented (see Scheme 2).



**Scheme 1.** Formula structures of  $Ag^+$  and  $Cu^{2+}$  salts of 5-nitrotetrazole (**1** and **2**) and their ethylenediamine adducts (**3** and **4**).

## Materials and Methods

**Caution!** Tetrazoles and their derivatives are energetic materials that tend to explode under certain conditions. Although we experienced no difficulties during the preparation and handling of the compounds described below, they are nevertheless energetic materials and their synthesis should only be carried out by experienced personnel. In particular the synthesis of compounds **1**, **2** and **5** should be only undertaken with proper protective measures such as wearing Kevlar gloves, ear protection, safety shoes and using plastic spatulas.

**General.** All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich Inc. and used as supplied. 5-Amino-1*H*-tetrazolium bromide [12], 1,3-dimethyl-5-aminotetrazolium iodide [11a] and silver 5-nitrotetrazolate [9] were prepared as described in the literature. <sup>1</sup>H (ref. TMS), <sup>13</sup>C (ref. TMS), and <sup>14</sup>N (ref. CH<sub>3</sub>NO<sub>2</sub>) NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-*d*<sub>6</sub> at 25 °C. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR instrument as KBr pellets at room temperature. Raman spectra were recorded on a Perkin-Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported in percentages relative to the most intense peak and are given in parentheses. Melting points were determined by differential scanning calorimetry (Linseis DSC PT-10 instrument, calibrated with standard pure indium and zinc). Measurements were performed in aluminium containers with a hole (1 mm) on the top for gas release with a nitrogen flow of 20 mL/min. The reference sample was a closed aluminum container.

**Synthesis of silver 5-nitrotetrazolate (1):** Sodium 5-nitrotetrazolate dihydrate (0.173 g, 1.00 mmol) [13] was dissolved in 10 mL water and a small excess of silver nitrate was added portion-wise (0.187 g, 1.10 mmol) causing the precipitation of a white powder. The reaction mixture was carefully (i.e., slow stirring rate) stirred for 30 minutes under the exclusion of light and the insoluble solid was filtered off, washed with water and left to air-dry (0.212 g, 95%). CN<sub>5</sub>O<sub>2</sub>Ag (221.91 g mol<sup>-1</sup>, calc./found): C 5.41 / 5.22, H - / 0.04, N 31.56 / 31.42, Ag 48.61 / 48.25%; DSC (5 °C/min, °C): 273 (dec.); m/z (FAB<sup>-</sup>, xenon, 6 keV, m-NBA matrix): 114.0 [CN<sub>5</sub>O<sub>2</sub>]<sup>-</sup>; Raman  $\tilde{\nu}$  / cm<sup>-1</sup> (rel. int.): 1567(5) 1432(100) 1414(50) 1330(21) 1203(32) 1089(34) 1070(58) 1017(12) 837(18) 738(2) 545(9) 256(2) 168(7); IR  $\tilde{\nu}$  / cm<sup>-1</sup> (KBr, rel. int.): 1648(w) 1537(vs) 1508(w) 1446(m) 1422(s) 1384(m) 1319(m) 1187(w) 1170(w) 1060(w) 1050(w) 1035(w) 841(m) 669(w) 476(w).

**Synthesis of copper(II) 5-nitrotetrazolate 5-nitrotetrazole dihydrate (2):** a small amount of **2** was isolated during the synthesis of sodium 5-nitrotetrazolate

dihydrate [13] and carefully (i.e., the compound was handled gently with a plastic spatula) analyzed.  $C_3H_5N_{15}O_8Cu$  (441.97 g mol<sup>-1</sup>, calc./found): C 8.14 / 7.91, H 1.14 / 1.29, N 47.52 / 47.41, Cu 14.24 / 13.88%; DSC (5 °C/min, °C): ~230 (dec.); Raman  $\tilde{\nu}$  / cm<sup>-1</sup> (rel. int.): 3063(2) 2822(26) 1885(30) 1871(33) 1435(100) 1130(56) 776(44) 420(46); IR  $\tilde{\nu}$  / cm<sup>-1</sup> (KBr, rel. int.): 3565(s) 3478(m) 1614(w) 1565(vs) 1445(m) 1435(m) 1384(m) 1328(m) 1236(w) 1065(w) 842(s) 664(w) 565(w) 475(w).

**Synthesis of silver(ethylenediamine) 5-nitrotetrazolate (3):** Sodium 5-nitrotetrazolate dihydrate (0.173 g, 1.00 mmol) was dissolved in 5 mL ethanol and a solution of ethylenediamine (0.085 g, 1.41 mmol) in 2 mL ethanol were added at 60 °C. The solution was heated to boiling and a saturated solution of silver nitrate (0.170 g, 1.00 mmol) in 10 mL hot ethanol was added slowly. The solution turned brown immediately and it was stirred at reflux for 2.5 hours. After this time, the brown precipitate which had formed was filtered off and discarded yielding a clear colourless solution from which crystals separated out on cooling (0.221 g, 78%).  $C_3H_8N_7O_2Ag$  (282.01 g mol<sup>-1</sup>, calc./found): C 12.78 / 12.68, H 2.86 / 2.77, N 34.77 / 34.59, Ag 38.25 / 37.91%; DSC (5 °C/min, °C): 108.1 (-en), ~212 (dec.); m/z (FAB<sup>+</sup>, xenon, 6 keV, m-NBA matrix): 60.1 [Ag(en)]<sup>+</sup>; m/z (FAB<sup>-</sup>, xenon, 6 keV, m-NBA matrix): 114.0 [CN<sub>5</sub>O<sub>2</sub>]<sup>-</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400.18 MHz, 25°C, TMS) δ/ppm: 3.4 (s, 4H, NH<sub>2</sub>), 2.7 (s, 4H, CH<sub>2</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 100.63 MHz, 25°C, TMS) δ/ppm: 168.4 (1C, C-NT), 43.3 (2C, CH<sub>2</sub>); <sup>14</sup>N {<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 40.55 MHz, 25 °C, MeNO<sub>2</sub>) δ/ppm: +19 (2N, ν<sub>1/2</sub> ~420 Hz, N2/3), -21 (1N, ν<sub>1/2</sub> ~60 Hz, NO<sub>2</sub>), -62 (2N, ν<sub>1/2</sub> ~400 Hz, N1/4); Raman  $\tilde{\nu}$  / cm<sup>-1</sup> (rel. int.): 3284(3) 2986(36) 2946(5) 2877(1) 1600(3) 1534(7) 1453(6) 1444(6) 1407(100) 1371(7) 1309(5) 1239(4) 1161(5) 1121(3) 1069(5) 1050(36) 1029(43) 1003(5) 845(5) 832(9) 769(2) 537(3) 449(3) 262(3) 239(5); IR  $\tilde{\nu}$  / cm<sup>-1</sup> (KBr, rel. int.): 3427(s) 3308(s) 1587(m) 1543(s) 1484(m) 1444(m) 1419(m) 1384(m) 1318(m) 1172(w) 1078(w) 1001(w) 840(m) 670(w) 522(w).

**Synthesis of bis(ethylenediamine)copper(II) 5-nitrotetrazolate (4):** Sodium 5-nitrotetrazolate dihydrate (0.177 g, 1.02 mmol) was dissolved in 10 mL ethanol and a solution of ethylenediamine (0.100 g, 1.67 mmol) in 5 mL ethanol was added dropwise under stirring at room temperature. The solution was heated to 70 °C and a solution of copper(II)chloride (0.068 g, 0.51 mmol) in 5 mL ethanol was added causing immediate precipitation of a blue-lilac solid. The reaction mixture was boiled for 1 hour and the lilac precipitate was filtered off and boiled again in fresh ethanol. Lastly, it was filtered off, washed with boiling ethanol and ether and left to air-dry yielding the title compound (0.163 g, 77%). Crystals suitable for X-ray analysis were obtained when an aqueous solution of the compound was left to slowly evaporate.  $C_6H_{16}N_{14}O_4Cu$

(411.83 g mol<sup>-1</sup>, calc./found): C 17.51 / 17.37, H 3.92 / 3.84, N 47.69 / 47.85, Cu 15.31 / 15.02%; DSC (5 °C/min, °C): ~225 (dec.); m/z (FAB<sup>+</sup>, xenon, 6 keV, m-NBA matrix): 183.2 [Cu(en)<sub>2</sub>]<sup>2+</sup>; m/z (FAB<sup>-</sup>, xenon, 6 keV, m-NBA matrix): 114.1 [CN<sub>5</sub>O<sub>2</sub>]<sup>-</sup>; Raman  $\tilde{\nu}$  / cm<sup>-1</sup> (rel. int.): 3282(3) 2956(4) 1605(4) 1535(7) 1460(8) 1442(6) 1407(100) 1319(7) 1284(5) 1174(3) 1155(4) 1113(7) 1054(42) 1032(44) 886(10) 862(3) 839(12) 774(2) 537(6) 476(8) 448(3) 299(7) 245(15); IR  $\tilde{\nu}$  / cm<sup>-1</sup> (KBr, rel. int.): 3450(s) 3331(vs) 3278(s) 3154(m) 2979(m) 2966(m) 2893(w) 2439(w) 1593(m) 1537(vs) 1504(w) 1459(w) 1441(s) 1410(s) 1384(m) 1316(m) 1281(w) 1268(w) 1172(w) 1155(w) 1084(w) 1053(w) 1033(s) 969(w) 839(m) 719(w) 669(w) 536(m) 471(w).

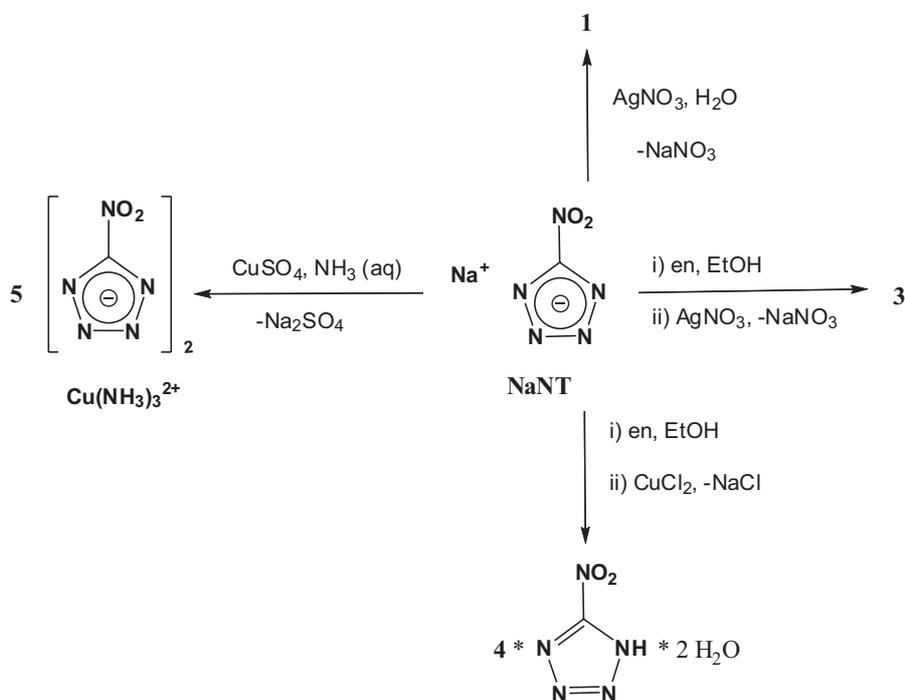
**Synthesis of triaminocopper(II) 5-nitrotetrazolate (5):** Sodium 5-nitrotetrazolate dihydrate (0.346 g, 2.00 mmol) was dissolved in 3 mL of 35% ammonia and slowly added to a solution of copper(II) sulphate (0.160 g, 1.00 mmol) in 3 mL 35% ammonia. After refluxing the reaction mixture for 15 minutes and stirring for a further 1 hour at room temperature a blue solid precipitated that was filtered off, washed with water and ethanol and left to air-dry (0.269 g, 79%). C<sub>2</sub>H<sub>9</sub>N<sub>13</sub>O<sub>4</sub>Cu (342.02 g mol<sup>-1</sup>, calc./found): C 7.02 / 7.07, H 2.65 / 2.75, N 53.22 / 53.38, Cu 18.40 / 18.12%; DSC (5 °C/min, °C): ~245 (dec.); m/z (FAB<sup>+</sup>, xenon, 6 keV, m-NBA matrix): 177.6 [Cu(CN<sub>5</sub>O<sub>2</sub>)<sup>+</sup>]; m/z (FAB<sup>-</sup>, xenon, 6 keV, m-NBA matrix): 114.1 [CN<sub>5</sub>O<sub>2</sub>]<sup>-</sup>, 405.7 [Cu(CN<sub>5</sub>O<sub>2</sub>)<sub>3</sub>]<sup>-</sup>; Raman  $\tilde{\nu}$  / cm<sup>-1</sup> (rel. int.): 3351(3) 3282(12) 1540(10) 1445(15) 1416(100) 1317(6) 1236(2) 1098(10) 1056(52) 1031(37) 839(14) 772(3) 536(5) 449(4) 415(5) 264(4); IR  $\tilde{\nu}$  / cm<sup>-1</sup> (KBr, rel. int.): 3355(s) 3278(m) 2846(w) 1612(m) 1538(vs) 1504(w) 1442(s) 1427(m) 1416(s) 1384(m) 1318(s) 1264(s) 1247(s) 1213(w) 1186(w) 1151(w) 1054(w) 1034(w) 1021(w) 840(s) 772(w) 701(m) 684(m) 667(m) 534(w).

**Synthesis of 5-amino-1*H*-tetrazolium 5-nitrotetrazolate (6):** An improved method to that reported in Ref. 11a is presented here. 5-Amino-1*H*-tetrazolium bromide (1–10 mmol) was dissolved in water and added to a suspension of **3** (1.0 eq) in the same solvent. Immediate precipitation of yellow silver bromide was observed and the reaction mixture was stirred for 0.5–2.0 h under the exclusion of light. After this time the solvent was carefully evaporated under vacuum at 50 °C leaving an off-white solid (quant. yield). C<sub>2</sub>H<sub>4</sub>N<sub>10</sub>O<sub>2</sub> (200.12 g mol<sup>-1</sup>, calc./found): C 12.00 / 11.73, H 2.01 / 1.72, N 69.99 / 69.45%; mp (uncorrected): 157.0–158.7 °C (Lit. 159 °C).

**Synthesis of 1,3-dimethyl-5-aminotetrazolium 5-nitrotetrazolate (7):** An improved method to that reported in Ref. 11b is presented here. **7** was obtained as described for **6** from 1,3-dimethyl-5-aminotetrazolium iodide and **3** in an improved 94% yield. C<sub>4</sub>H<sub>8</sub>N<sub>10</sub>O<sub>2</sub> (228.17 g mol<sup>-1</sup>, calc./found): C 21.05 / 20.84, H 3.53 / 3.32, N 61.39 / 61.07%; mp (uncorrected): 160.0–161.4 °C (Lit. 160.5 °C).

## Results and Discussion

The ligand-free copper salt (**2**) was prepared according to a known literature procedure and only a small amount of the compound was isolated for analysis due to its highly sensitive nature [7b]. **2** was treated as the wet cake to synthesize sodium 5-nitrotetrazolate dihydrate (NaNT) according to a recently reported protocol from our group [13]. NaNT was used as the starting material for the synthesis of compounds **1**, **3**, **4** and **5** (Scheme 2). Reaction of NaNT with silver nitrate in aqueous solution resulted in the precipitation of highly sensitive **1**. An analogous reaction using ethanol as the solvent and in the presence of a  $\text{Ag}^+$  or  $\text{Cu}^{2+}$  salt and ethylenediamine, yielded the much less sensitive ethylenediamine adducts **3** and **4**, respectively. Lastly, salt **5** was prepared by the reaction of NaNT with a  $\text{Cu}^{2+}$  salt in aqueous ammonia.

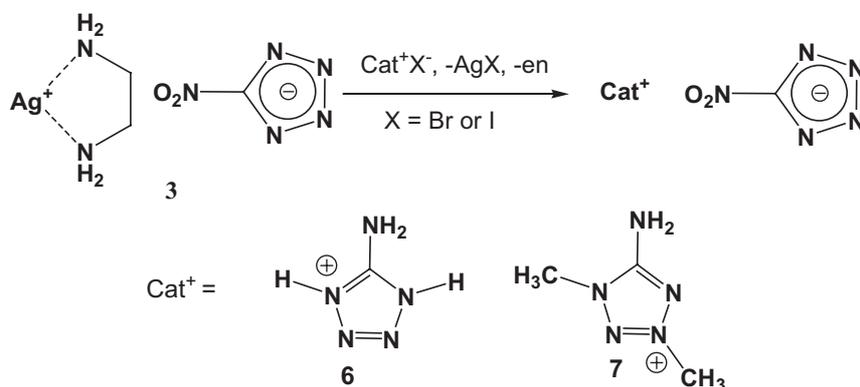


**Scheme 2.** Synthesis of the 5-nitrotetrazolate salts in this study.

Special care must be taken, in particular when handling the ethylenediamine-free compounds **1**, **2** and **5** since they are extremely sensitive materials and accidental explosion might occur (see discussion below).

Compounds **1**, **2** and **5** are highly insoluble in most polar solvents and dissolve to a low extent in coordinating solvents such as concentrated ammonia or pyridine. On the other hand, the ethylenediamine adducts **3** and **4** are soluble in polar solvents such as ethanol, water or DMSO and insoluble in less polar or apolar solvents such as acetone, acetonitrile, ether or chloroform.

To proof the suitability of the compounds synthesized for a safe transfer of the NT anion, compound **3** was reacted with 5-amino-1*H*-tetrazolium bromide and with 1,3-dimethyl-5-aminotetrazolium iodide to yield two previously reported tetrazolium salts (see Scheme 3). [11a, 11b] Both compounds were synthesized in a 1 to 10 mmol scale in yields higher than 90% providing a safe up-scalable synthesis for compounds **6** and **7**.



**Scheme 3.** Safe transfer of the NT anion as exemplified by the synthesis of tetrazolium salts **6** and **7**.

Microcrystals of the Ag<sup>+</sup> salt **3** separated out of the hot ethanolic mixture upon cooling (see experimental part above). However, they presented twinning problems and a satisfactory structure could not be obtained. On the other hand, crystals of the purple compound **4** (obtained as described above) suitable for X-ray structure analysis could be grown. The data collection of **4** was performed using the CrysAlis CCD software [14], and the data reduction was performed with the CrysAlis RED software [15]. The structure was solved by direct methods using the standard software implemented in the WinGX package [16-19] and finally checked with PLATON [20]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from difference Fourier electron density maps and refined isotropically. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method [21]. Table 1 tabulates the structure solution and refinement data for compound **4**.

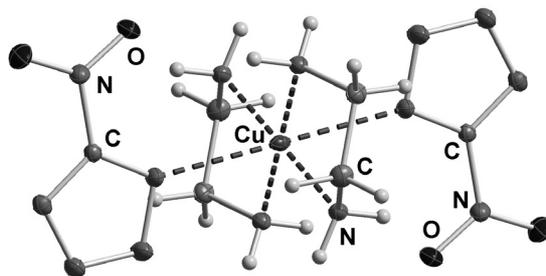
**Table 1.** Crystal data and structure refinement for Cu<sup>2+</sup> salt **4**

Parameter	<b>4</b>
Empirical formula	C <sub>6</sub> H <sub>16</sub> N <sub>14</sub> O <sub>4</sub> Cu
Formula weight [g mol <sup>-1</sup> ]	411.87
Temperature / K	100
Crystal system	orthorhombic
Space group	Pbca
<i>a</i> / Å	7.5200(1)
<i>b</i> / Å	14.0124(2)
<i>c</i> / Å	14.7740(2)
$\alpha$ / °	90
$\beta$ / °	90
$\gamma$ / °	90
<i>V</i> <sub>UC</sub> / Å <sup>3</sup>	1556.78(4)
<i>Z</i>	4
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.757
<i>m</i> / mm <sup>-1</sup>	1.455
<i>F</i> (000)	844
$\Theta$ range / °	3.87–30.11
Index ranges	-10 < <i>h</i> < 10 -19 < <i>k</i> < 19 -20 < <i>l</i> < 20
Reflections collected	18690
Independent reflections	2290
Data/Restraints/ Parameters	2290/0/147
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.184
<i>R</i> <sub>int</sub>	0.0292
<i>R</i> <sub>1</sub> [ <i>F</i> > 4σ( <i>F</i> )]	0.0302
<i>R</i> <sub>1</sub> (all data)	0.0448
w <i>R</i> <sub>2</sub> [ <i>F</i> > 4σ( <i>F</i> )]	0.0606
w <i>R</i> <sub>2</sub> (all data)	0.0710

$${}^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad {}^b R_w = [\Sigma (F_o^2 - F_c^2) / \Sigma w (F_o^2)]^{1/2}. \quad {}^c w = [\sigma_c^2 (F_o^2) + (xP)^2 + yP]^{-1}, \quad P = (F_o^2 - 2F_c^2) / 3.$$

Figure 1 shows a view of the coordination around the Cu<sup>2+</sup> cation in the crystal structure of compound **4**. Within the limits of error the bond distances and angles around the NT anions are essentially identical to those found in recently reported heterocycle- and metal-based salts with the same anion [11e, 13]. The

geometry around the  $\text{Cu}^{2+}$  cations is that of a distorted octahedron with four very similar long distances of ca. 2.02 Å to the ethylenediamine ligands and two longer distances at ca. 2.58 Å to the two NT anions, making for an elongated octahedron. The small Jahn-Teller effect found in the coordination geometry is manifested in angles very close to the ideal 90 and 180°. The structure is held together by a total of six weak hydrogen-bonds formed by the amino groups of the ethylenediamine ligands.



**Figure 1.** Asymmetric unit of  $\text{Cu}^{2+}$  salt **4** showing the octahedral coordination around the cation.

The vibrational modes of the anion in the IR and Raman spectra of the compounds can be conveniently assigned by comparison with the calculated values [11e]. Compounds **1** and **2** show the characteristic coupled  $\text{NO}_2$  and  $\text{N1-C-N4}$  stretching vibration both in the Raman (ca. 1430  $\text{cm}^{-1}$ ) and in the IR (ca. 1425  $\text{cm}^{-1}$ ) spectra. On the other hand, salts **3-5** exhibit a bathochromic shift of this coupled vibration down to ca. 1410  $\text{cm}^{-1}$ .

Due to the paramagnetism of  $\text{Cu}^{2+}$  and the high insolubility of compound **1**, only the NMR of salt **3** could be recorded. The  $^1\text{H}$  NMR spectrum of this compound shows only the resonances of the ethylenediamine ligand at 3.4 and 2.7 ppm for the amino and the methylene groups, respectively. In the  $^{13}\text{C}$  NMR spectrum the ligand resonances appear at 43.3 ppm and the quaternary carbon of the NT anion, shows a low intensity signal at 168.4 ppm, in keeping with the sodium salt ( $\text{NaNT}$ ) [13]. Lastly, the  $^{14}\text{N}$  NMR resonances are also in agreement with those of  $\text{NaNT}$ . They are observed at +19 (N2/N3), -21 ( $\text{NO}_2$ ) and -62 (N1/N4) ppm.

Due to the interest of compounds **1-5** as energetic materials, the energetic properties of all five compounds were assessed by testing their response to fast heating, evaluating their sensitivities towards impact, friction and electrostatic discharge and determining their thermal stability by DSC (differential scanning calorimetry) analysis. The results of these tests have been collected in Table 2 and

the values for commonly used lead(II) azide have been included for comparison purposes.

**Table 2.** Energetic properties of compounds **1-5** and comparison with lead azide

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	Pb(N <sub>3</sub> ) <sub>2</sub>
Formula	CN <sub>5</sub> O <sub>2</sub> Ag	C <sub>3</sub> H <sub>5</sub> N <sub>15</sub> O <sub>8</sub> Cu	C <sub>3</sub> H <sub>8</sub> N <sub>7</sub> O <sub>2</sub> Ag	C <sub>6</sub> H <sub>16</sub> N <sub>14</sub> O <sub>4</sub> Cu	C <sub>2</sub> H <sub>9</sub> N <sub>13</sub> O <sub>4</sub> Cu	N <sub>6</sub> Pb
MW	221.91	441.47	282.01	411.83	342.02	291.24
<i>T</i> <sub>m</sub> (°C) <sup>a</sup>	–	–	–	–	–	–
<i>T</i> <sub>dec</sub> (°C) <sup>b</sup>	273	230	212	225	245	315–360 <sup>b</sup>
<i>N</i> (%) <sup>c</sup>	31.56	51.66	34.77	47.62	53.22	28.86
<i>Ω</i> (%) <sup>d</sup>	–7.2	–5.9	–51.1	–66.0	–25.7	–5.5
Impact (J) <sup>e</sup>	<1	<3	>40	<7	<2	2.5–4.0 <sup>f</sup>
Friction (N) <sup>e</sup>	<5	<5	<240	<252	<18	0.1–1.0 <sup>f</sup>
ESD (+/–) <sup>f</sup>	+	+	–	–	–	+
Thermal Shock <sup>g</sup>	Explodes	Explodes	Explodes	Explodes	Explodes	Explodes

<sup>a,b</sup> Melting and decomposition points (onset from DSC experiments at  $\beta = 5$  °C min<sup>–1</sup> (compounds **1-5**) and from Ref. [22] (lead azide). <sup>c</sup> Percentage of nitrogen in the molecule. <sup>d</sup> Oxygen balance calculated according to Ref. [23]. <sup>e</sup> BAM methods were used to determine the impact and friction sensitivities of the compounds. [24–26] <sup>f</sup> Rough sensitivity to a 20 kV electrostatic discharge from an HF-Vacuum-Tester type VP 24 (ESD testing): + sensitive, – insensitive. <sup>g</sup> A few milligrams of the compound were loaded on a metal spatula and heated using a *Bunsen* burner <sup>h</sup> At 360 °C lead azide deflagrates. <sup>i</sup> The sensitivity values for lead azide were determined for the technically pure compound.

When compounds **1-5** were heated rapidly, the result was a loud explosion for all five compounds, similar as for lead azide. Compounds **1** and **2** tested to be more impact sensitive and possibly more friction sensitive than lead azide, however compound **5** was very impact sensitive but less friction sensitive. These results are in contrast with the relatively low sensitivities of the ethylenediamine adducts **3** and **4** towards impact and friction. The lower sensitivity of compounds **3**, **4** and **5** towards impact and friction also seems to correlate well with the lower sensitivities towards electrostatic discharge of these salts in comparison to highly sensitive **1**, **2** and lead azide. Salts **3**, **4** and **5** failed to give an explosion in the electrostatic-discharge tester, whereas testing **1** and **2** lead to loud explosions as would be expected from lead azide. DSC analysis did not show a defined melting point for any of the compounds **1-5** and sharp exothermic decomposition was observed above 200 °C. The decomposition points of these materials are higher than those of heterocycle-based salts with the same anion [11e] and comparable to those of alkali metal salts [13]. Here it is important to note that Cu<sup>2+</sup> salts **2** and **5** showed LIC (laser initiation capability), i.e., both compounds were initiated by a laser beam of ca. 300 mW during the Raman measurements.

## Conclusions

Compounds **1** and **2** are useful starting materials for the synthesis of salts with the 5-nitrotetrazolate (NT) anion. However, their high sensitivity towards classical stimuli limits their use on a large scale. We have prepared two ethylenediamine adducts containing the NT anion (**3** and **4**), which are much safer to handle and exemplified the use of **3** for the synthesis of two tetrazolium salts containing the NT anion. Additionally, we synthesized a Cu<sup>2+</sup> ammonia adduct of the NT anion (**5**), which shows decreased sensitivity towards friction in comparison to commonly used lead azide. Lastly, **5** has the particularity that can be conveniently initiated by impact or by a laser beam and in the absence of a toxic metal, might provide an improved alternative to lead azide in initiating devices.

## Acknowledgements

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Fonds der Chemischen Industrie (FCI), the European Research Office (ERO) of the U.S. Army Research Laboratory (ARL) and ARDEC (Armament Research, Development and Engineering Center) under contract Nos. N 62558-05-C-0027, R&D 1284-CH-01, R&D 1285-CH-01, 9939-AN-01 & W911NF-07-1-0569 and the Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants (WIWEB) under contract Nos. E/E210/4D004/X5143 & E/E210/7D002/4F088 is gratefully acknowledged. The authors acknowledge collaborations Dr. M. Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. M. Sucasca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation parameters of high-nitrogen explosives. We are indebted to and thank Dr. Betsy M. Rice (ARL, Aberdeen, Proving Ground, MD) for many helpful and inspired discussions and support of our work.

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