



5-Aminotetrazoles and Silver-based Primary Explosives

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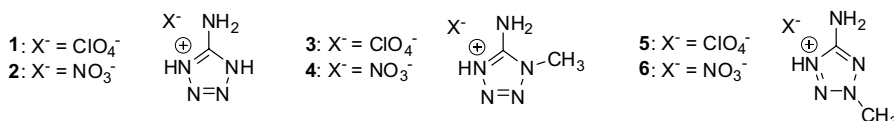
Abstract: Several silver nitrate and perchlorate salts with 5-aminotetrazole-based ligands have been synthesized and characterized by elemental analysis, mass spectrometry, IR, Raman and multinuclear NMR spectroscopy. In addition, several of the new compounds were characterized by X-ray structure analysis. The energetic properties of the materials were assessed by differential scanning calorimetry (DSC) analysis in combination with standard impact and friction BAM tests. The compounds synthesized have good thermal stabilities above 225 °C and in some instances the high sensitivities of the materials towards impact and friction make them fall under the category of primary explosives. Some of the compounds might present prospective use in initiation devices for civil and military applications.

Keywords: silver, nitrogen-heterocycles, primary explosives, BAM tests

Introduction

Primary explosives are energetic materials, in which detonation is easily initiated by a physical or electrical stimulus. They are used in small amounts in order to initiate less sensitive but more powerful secondary explosives. Mercury fulminate is one of the first primary explosives, which has been used in history however due to its high sensitivity it was replaced by lead diazide [1, 2]. A major issue for the application of primary explosives is to find a candidate, which is

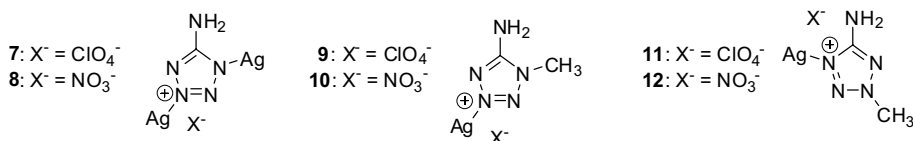
sensitive enough to be initiated when desired but not too sensitive that it initiates accidentally. In this context, lead azide has the drawback of being very sensitive to friction, electrostatic discharge and impact in addition to being highly toxic due to the metal.



Scheme 1. Structural formulas of protonated 5-aminotetrazolium salts [4, 5].

In this line, we recently investigated the potential of alkali metal salts with the 5-nitrotetrazolate anion as primary explosives [3] and were, in light of their promising properties, interested in investigating the potential of new tetrazole-based compounds with silver cations as primary explosives. These compounds are reminiscent of our recently reported protonated 5-aminotetrazolium salts (see Scheme 1), in which the protons have been exchanged by silver cations [4, 5].

Although several metal tetrazolate salts have been described in the literature, [6-9] many do not show prospective interest in the field of energetic materials. However, the compounds presented here represent some of the first examples of metal compounds containing a tetrazole moiety with prospective interest for use in energetic applications.



Scheme 2. Structural formulas of silver-substituted 5-aminotetrazolium salts.

Materials and Methods

Cautionary Note: Many of the compounds used in this study are sensitive energetic materials and should only be synthesized and manipulated on a small (<250 mg) scale using proper safety equipment including, but not limited to, thick leather or Kevlar gloves, leather or Kevlar jackets, face shields and blast screens, ear plugs and plastic or Teflon laboratory equipment.

All chemical reagents and solvents were obtained from Sigma Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied. 1-Methyl- and

2-methyl-5-amino-1*H*-tetrazole, [10] and 5-amino-1*H*-tetrazolium perchlorate (**1**) [11] were prepared by previously reported procedures. ^1H , ^{13}C , ^{14}N and ^{35}Cl NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO- d_6 at room temperature. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR instrument as KBr pellets at 20 °C. Transmittance values are qualitatively described as ‘very strong’ (vs), ‘strong’ (s), ‘medium’ (m) and ‘weak’ (w). 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 as percentages of the most intense peak and are given in parentheses. Elemental analyses were performed on a Netsch Simultaneous Thermal Analyzer STA 429. Mass spectra were measured on a JEOL MStation JMS 700 instrument. Melting and decomposition points were determined by differential scanning calorimetry (Perkin-Elmer Pyris 6 DSC instrument) at a heating rate of 5 °C min $^{-1}$ closed in aluminum sample pans with a 1 mm hole in the top for gas release under a nitrogen flow of 20 mL min $^{-1}$.

Synthesis of Disilver 5-Amino-1*H*-tetrazolium Perchlorate (7): 5-Amino-1*H*-tetrazolium monohydrate (0.196 g, 1.8 mmol) was dissolved in 4 mL concentrated perchloric acid and a solution of silver perchlorate (0.377 g, 1.8 mmol) in 1.5 mL water was added dropwise (cloudiness in the solution was observed as the addition proceeded). The clear solution was stirred for 30 minutes before adding 10 mL water. Immediate precipitation of a white (**highly sensitive!!**) powder was observed and the reaction mixture was stirred for further 15 minutes before filtering the solid by gravity. This was washed five times with water, one time with iso-propanol and one time with ether and left to air-dry overnight. The product was carefully weighed (0.522 g, 73%). DSC (5 °C min $^{-1}$, °C): 319 (dec.); IR $\tilde{\nu}$ / cm $^{-1}$ (KBr, rel. int.): 3414(s) 3326(vs) 3228(m) 2285(w) 1617(s) 1557(s) 1542(s) 1458(m) 1439(w) 1384(w) 1268(w) 1143(s) 1113(vs) 1086(vs) 940(w) 920(w) 768(w) 742(w) 703(w) 636(m) 625(m) 573(w) 460(w) 430(w); Raman $\tilde{\nu}$ / cm $^{-1}$ (rel. int.): 3332(8) 1637(10) 1562(36) 1464(22) 1437(11) 1403(8) 1281(55) 1256(28) 1235(24) 1150(57) 1125(86) 1102(59) 1026(23) 930(100) 769(40) 625(27) 464(38) 349(10) 166(28); $\text{CH}_2\text{N}_5\text{O}_4\text{ClAg}_2$ (399.25 g mol $^{-1}$, calc./found): C 3.02 / 2.88, H 0.51 / 0.72, N 17.65 / 17.90, Ag 53.89 / 53.60%.

Synthesis of Disilver 5-Amino-1*H*-tetrazolium Nitrate (8): To a suspension of 5-amino-1*H*-tetrazolium monohydrate (0.503 g, 4.9 mmol) in 10 mL concentrated nitric acid was added dropwise a solution of silver nitrate (0.832 g, 4.9 mmol) in 3 mL water. The reaction mixture was stirred for 45 minutes and 10 mL water were added. After a few seconds cloudiness in the solution was observed and after 15 minutes a white powder precipitated,

which was filtered off under gravity (**very sensitive compound!!**) and washed thoroughly with isopropanol and ether. The product was left to air-dry on a filter paper (1.423 g, 80%). DSC (5 °C min⁻¹, °C): 298 (dec.); IR $\tilde{\nu}$ / cm⁻¹ (KBr, rel. int.): 3416(s) 3326(s) 3227(m) 2396(w) 1762(w) 1620(m) 1541(m) 1454(m) 1434(m) 1384(vs) 1282(m) 1189(w) 1173(w) 1153(m) 1113(w) 1038(w) 1021(w) 833(w) 824(w) 816(w) 769(w) 747(w) 567(w) 461(w) 431(w); Raman $\tilde{\nu}$ / cm⁻¹ (rel. int.): 1623(9) 1543(8) 1389(6) 1295(28) 1164(13) 1109(53) 1040(100) 779(16) 710(7) 459(10) 184(25); CH₂N₆O₃Ag₂ (359.83 g mol⁻¹, calc./found): C 3.33 / 3.13, H 0.56 / 0.78, N 23.35 / 23.60, Ag 59.42 / 59.42%.

Synthesis of silver 1-methyl-5-amino-1H-tetrazolium perchlorate hemihydrate (9): The perchlorate salt was synthesized in analogy to the nitrate derivative from 1-methyl-5-amino-1H-tetrazole (0.179 g, 1.8 mmol) in 3 mL concentrated perchloric acid by reaction with a solution of silver perchlorate (0.398 g, 1.9 mmol) in 3 mL water yielding a white powder of pure material (0.342 g, 63%). Recrystallization from hot water afforded single crystals of the compound in high yield. DSC (5 °C min⁻¹, °C): 102 (–H₂O), 154 (m.p.), 252 (dec.); ¹H NMR ([D6]DMSO, 400.18 MHz, 25°C, TMS) δ /ppm: 7.02 (2H, s, NH₂), 3.74 (3H, s, CH₃); ¹³C {¹H} NMR ([D6]DMSO, 100.63 MHz, 25°C, TMS) δ /ppm: 30.1 (CH₃), 155.6 (C–NH₂); ³⁵Cl NMR ([D6]DMSO, 39.21 MHz, 25 °C, NaCl) δ /ppm: +1000 (ClO₄⁻); IR $\tilde{\nu}$ / cm⁻¹ (KBr, rel. int.): 3326(s) 3155(vs) 2951(m) 2742(w) 1669(vs) 1596(s) 1485(m) 1454(w) 1428(w) 1384(w) 1322(m) 1280(w) 1237(w) 1144(s) 1120(s) 1088(s) 970(w) 940(w) 790(m) 742(w) 707(w) 680(m) 669(w) 636(m) 626(m) 544(m); Raman $\tilde{\nu}$ / cm⁻¹ (rel. int.): 3014(8) 2956(26) 1658(13) 1595(9) 1499(12) 457(13) 1421(12) 1369(15) 1344(29) 1280(19) 1152(27) 1080(22) 929(89) 795(67) 684(21) 635(14) 622(18) 466(20) 449(20) 300(22) 248(13); m/z (FAB⁺, xenon, 6 keV, m-NBA matrix): 206.0 (8, [C₂H₄N₅Ag]) 208.0 (7, [C₂H₆N₅Ag]²⁺), 305.0 (10, [Ag(C₂H₅N₅)₂]⁺); C₂H₆N₅O_{4.5}ClAg (315.42 g mol⁻¹, calc./found): C 7.62 / 7.89, H 1.92 / 1.69, N 22.20 / 22.09, Ag 34.20 / 34.58%.

Synthesis of silver 1-methyl-5-amino-1H-tetrazolium nitrate (10): 1-Methyl-5-amino-1H-tetrazole (0.198 g, 0 mmol) was solvated in 3 mL concentrated nitric acid and a solution of silver nitrate (0.368 g, 2 mmol) in 4 mL water was added causing some cloudiness in the solution. The mixture was stirred for 20 minutes and the formed precipitate was filtered off under vacuum, washed with methanol, then with ether and dried under high vacuum yielding an insoluble white powder, which was pure as confirmed by elemental analysis (0.262 g, 48%). Recrystallization from hot water resulted in X-ray quality crystals of **13** and silver nitrate. DSC (5 °C min⁻¹, °C): 182 (m.p.), 226 (dec.); ¹H NMR ([D6]DMSO, 400.18 MHz, 25°C, TMS) δ /ppm: 7.01 (2H, s, NH₂), 3.74 (3H, s,

CH₃); ¹³C {¹H} NMR ([D₆]DMSO, 100.63 MHz, 25 °C, TMS) δ/ppm: 31.9 (CH₃), 155.7 (C–NH₂); ¹⁴N NMR ([D₆]DMSO, 40.51 MHz, 25 °C, CH₃NO₂) δ/ppm: –4.3 (1N, NO₃[–]); IR $\tilde{\nu}$ / cm^{–1} (KBr, rel. int.): 3402(m) 3323(s) 3265(m) 2948(w) 2192(m) 3157(s) 2950(w) 2426(w) 2345(w) 1767(w) 1747(w) 1667(s) 1648(s) 1595(s) 1494(m) 1384(vs) 1338(s) 1320(s) 1303(s) 1238(m) 1144(m) 1121(w) 1089(m) 1051(w) 1041(m) 984(w) 833(w) 825(w) 817(w) 788(m) 742(w) 736(w) 707(w) 679(m) 568(w) 483(w); Raman $\tilde{\nu}$ / cm^{–1} (rel. int.): 2986(22) 2960(16) 2798(5) 1652(57) 1497(60) 1416(62) 1339(66) 1281(62) 1144(59) 1082(57) 1043(100) 989(42) 791(70) 680(39) 481(31) 304(30); m/z (FAB⁺, xenon, 6 keV, m-NBA matrix): 206.0 (3, [C₂H₄N₅Ag]) 208.0 (3, [C₂H₆N₅Ag]²⁺), 305.0 (5, [Ag(C₂H₅N₅)₂]⁺); C₂H₅N₆O₃Ag (268.97 g mol^{–1}, calc./found): C 8.96 / 8.90, H 1.88 / 2.09, N 31.36 / 31.19, Ag 39.90 / 39.68%.

Synthesis of silver 2-methyl-5-amino-1H-tetrazolium perchlorate (11):

Anhydrous silver perchlorate (0.400 g, 1.9 mmol) (weighed in a glove-box) was dissolved in 3 mL water and added to a solution of 2-methyl-5-amino-1H-tetrazole (0.179 g, 1.8 mmol) in 2 mL 70% perchloric acid. After 15 minutes reaction time a white powder precipitated and the reaction mixture was shortly brought to reflux (not all solid dissolved). Single crystals of the title compound formed overnight upon cooling that were filtered off, washed thoroughly with acetone and ether and left to air-dry (0.357 g, 65%). DSC (5 °C min^{–1}, °C): 286 (m.p.), 289 (dec.); ¹H NMR ([D₆]DMSO, 400.18 MHz, 25 °C, TMS) δ/ppm: 6.1 (2H, s, NH₂), 4.1 (3H, s, CH₃); ¹³C {¹H} NMR ([D₆]DMSO, 100.63 MHz, 25 °C, TMS) δ/ppm: 39.0 (CH₃), 166.9 (C–NH₂); ³⁵Cl NMR ([D₆]DMSO, 39.21 MHz, 25 °C, NaCl) δ/ppm: +1000 (ClO₄[–]); IR $\tilde{\nu}$ / cm^{–1} (KBr, rel. int.): 3386(s) 3309(s) 3220(m) 3073(w) 2960(w) 2676(w) 2021(w) 1688(m) 1635(s) 1584(w) 1554(s) 1452(m) 1422(w) 1409(m) 1377(w) 1326(w) 1292(w) 1205(m) 1145(vs) 1112(vs) 1089(vs) 941(w) 809(w) 757(w) 707(m) 684(w) 668(w) 649(m) 636(s) 626(s) 488(w); Raman $\tilde{\nu}$ / cm^{–1} (rel. int.): 3246(20) 3223(20) 2962(69) 1647(24) 1578(25) 1444(27) 1378(31) 1196(28) 1169(20) 1119(38) 1036(30) 963(24) 926(100) 892(33) 812(22) 675(18) 649(47) 623(44) 594(21) 461(42) 429(22) 348(22) 250(19) 167(18) 150(20); m/z (FAB⁺, xenon, 6 keV, m-NBA matrix): 206.0 (6, [C₂H₄N₅Ag]) 208.0 (5, [C₂H₆N₅Ag]²⁺), 305.0 (7, [Ag(C₂H₅N₅)₂]⁺); C₂H₅N₅O₄ClAg (306.41 g mol^{–1}, calc./found): C 7.87 / 7.79, H 1.65 / 1.91, N 22.96 / 22.75, Cl 11.47 / 11.30, Ag 35.06 / 35.26%.

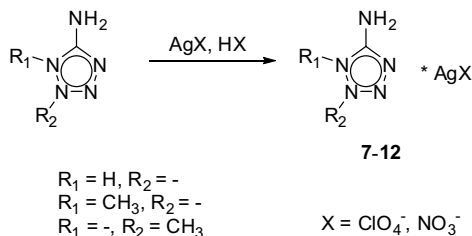
Synthesis of silver 2-methyl-5-amino-1H-tetrazolium nitrate (12):

2-Methyl-5-amino-1H-tetrazole (0.198 g, 0 mmol) was dissolved in 2 mL 65% nitric acid and a solution of silver nitrate (0.385 g, 3 mmol) in 3 mL water was added dropwise causing cloudiness in the solution. The cloudy solution was stirred for 15 minutes at room temperature causing precipitation of a white

powder and it was shortly brought to reflux. Lastly, 3 mL water were added to the reaction mixture at room temperature and this was left to stand. The powder that precipitated overnight was filtered off, washed thoroughly with acetone and ether and left to air-dry (0.333 g, 62%). DSC (5 °C min⁻¹, °C): 259 (m.p. + dec.); ¹H NMR ([D6]DMSO, 400.18 MHz, 25°C, TMS) δ/ppm: 6.0 (2H, s, NH₂), 4.0 (3H, s, CH₃); ¹³C {¹H} NMR ([D6]DMSO, 100.63 MHz, 25°C, TMS) δ/ppm: 38.8 (CH₃), 166.9 (C–NH₂); ¹⁴N NMR ([D6]DMSO, 40.51 MHz, 25 °C, CH₃NO₂) δ/ppm: –4.1 (1N, NO₃⁻); IR $\tilde{\nu}$ / cm⁻¹ (KBr, rel. int.): 3395(s) 3034(m) 2957(w) 2426(w) 1921(w) 1842(w) 1762(w) 1636(m) 1554(m) 1484(vs) 1436(m) 1423(m) 1384(vs) 1324(vs) 1273(s) 1210(s) 1122(m) 1094(vs) 1054(s) 1036(s) 1011(s) 881(s) 839(w) 808(w) 776(s) 760(s) 748(m) 701(s) 674(m) 649(w) 468(w); Raman $\tilde{\nu}$ / cm⁻¹ (rel. int.): 3215(4) 3045(6) 2987(100) 2921(6) 1590(11) 1533(58) 1526(51) 1509(22) 1471(22) 1423(15) 1391(18) 1363(15) 1256(13) 1225(18) 1082(12) 1047(89) 1011(19) 941(8) 875(7) 824(8) 760(19) 718(11) 455(14) 439(9) 399(9) 359(13) 275(8) 241(11); m/z (FAB⁺, xenon, 6 keV, m-NBA matrix): 206.0 (3, [C₂H₄N₅Ag]) 208.0 (3, [C₂H₆N₅Ag]²⁺), 305.0 (4, [Ag(C₂H₅N₅)₂]⁺); C₂H₅N₆O₃Ag (268.97 g mol⁻¹, calc./found): C 8.96 / 8.97, H 1.88 / 1.89, N 31.36 / 31.09, Ag 39.90 / 39.65%.

Results and Discussion

The silver salts described in this work (see Scheme 2) were prepared by reaction of the corresponding neutral 5-aminotetrazole, i.e., 5-amino-1*H*-tetrazole (At), 1-methyl-5-amino-1*H*-tetrazole (1MAT) and 2-methyl-5-amino-1*H*-tetrazole (2MAT) with a silver salt (i.e., silver nitrate or silver perchlorate) in an aqueous solution of the corresponding acid (i.e., nitric or perchloric acid). Addition of water and further stirring resulted in the precipitation of the compounds, which were carefully filtered, due to their high sensitivity towards impact and friction (!!).



Scheme 3. Synthesis of silver salts **7-12**.

Whereas perchlorate salt **9** turned out to be stable upon heating in water yielding single crystals of the compound after slow cooling and evaporation (see discussion below), recrystallization of the nitrate salt **10** from water lead to the formation of a new silver salt, namely tris-(1-methyl-5-amino-1*H*-tetrazole) silver nitrate (**13**), the structure of which is also described below.

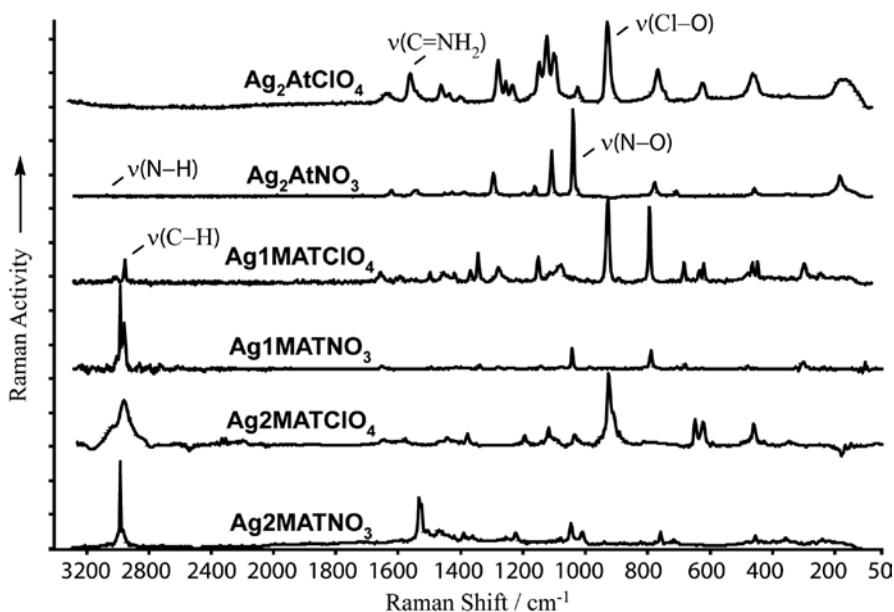


Figure 1. Panel plot of the Raman spectra of silver salts **7–12** (Ag^+ = silver cation, At = 5-amino-1*H*-tetrazole, 1MAT = 1-methyl-5-amino-1*H*-tetrazole, 2MAT = 2-methyl-5-amino-1*H*-tetrazole, NO_3^- = nitrate anion and ClO_4^- = perchlorate anion).

Both IR and Raman spectra of the nitrate and perchlorate salts of this study show the characteristic bands for the anions (IR (NO_3^-) at *ca.* 1385 cm^{-1} , Raman (NO_3^-) at *ca.* 1040 cm^{-1} and IR (ClO_4^-) at *ca.* 1090 cm^{-1} , Raman (ClO_4^-) at *ca.* 930 and *ca.* 460 cm^{-1}) [12, 13]. In addition, to the sharp and intense bands corresponding to the anion, the IR and Raman spectra of the compounds contain a set of bands of lower intensity, which fit very well with data available for protonated 5-amino-1*H*-tetrazolium salts [14, 15]. Figure 1 shows a panel plot of the Raman spectra of compounds **7–12** for illustration purposes.

No NMR data could be recorded on the disilver salts **7** and **8** due to their high insolubility in any solvent tried. However, the 1-methyl- and 2-methyl-5-

amino-1*H*-tetrazolium salts show ^1H NMR resonances at δ ca. 7.0 ppm and δ ca. 6.0 ppm (in DMSO- d_6), respectively for the protons of the amino groups. In comparison to the protonated tetrazolium salts **1** [15] and **2** [14] these resonances are shifted to high field, which is indicative of an increase of the basicity of these protons for the silver complexes. On the other hand, the protons of the methyl groups show resonances at δ ca. 3.7 ppm and δ ca. 4.0 ppm, for the 1-methyl- and 2-methyl-5-amino-1*H*-tetrazolium salts, respectively. In analogy to the ^1H NMR spectra, the tendency in the resonances of the silver salts in the ^{13}C NMR spectra is also to show at higher field [4]. The ^1H , ^{13}C and ^{14}N NMR spectra of compound **10** are depicted in Figure 2 as examples of the spectra of one of the silver salts in this work.

From the silver salts described in this study, single crystals suitable for X-ray analysis of compounds **9** and **12** were obtained as described in the experimental section. In addition, compound **10** rearranged to form the nitrate salt **13**, which was also characterized by X-ray diffraction experiments. The X-ray crystallographic data for all compounds were collected by using an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector with graphite-monochromated Mo K α radiation. All structures were solved by using direct methods (SHELXS-97 and SIR97) and refined by means of full-matrix least-squares procedures using SHELXL-97 [16, 17]. CCDC-693944 (**9**), -693945 (**12**) and -693947 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

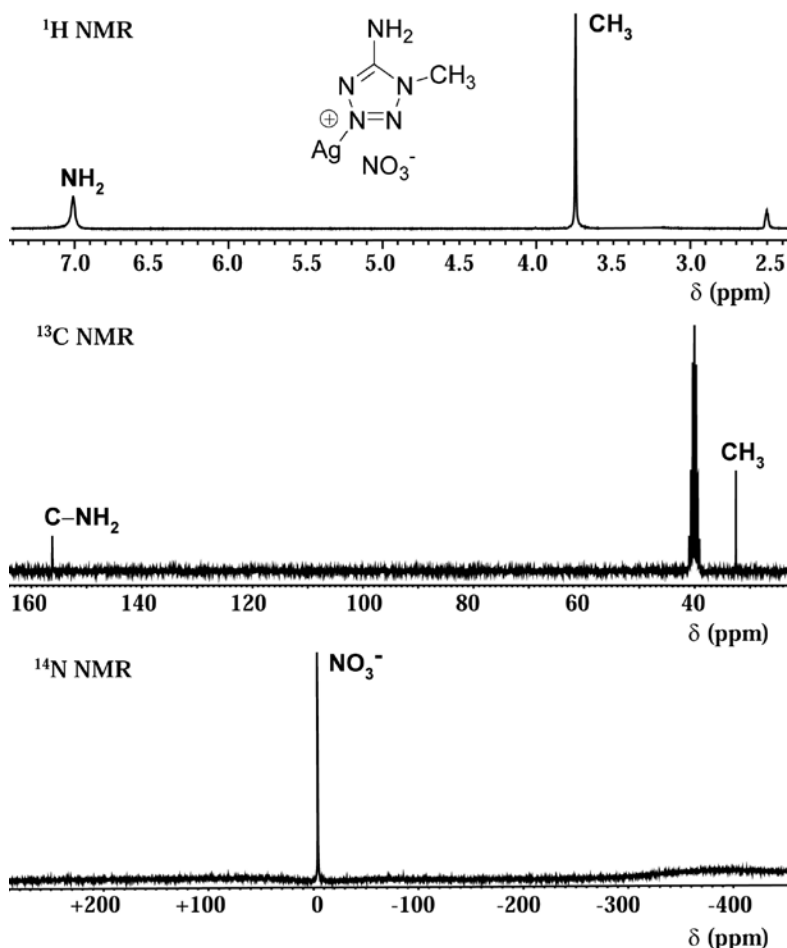


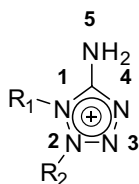
Figure 2. ^1H , ^{13}C and ^{14}N NMR spectra of nitrate salt **10** in DMSO-d_6 .

The data for the crystal structure solution and refinement for compounds **9**, **12** and **13** has been tabulated in Table 1. In addition, Table 2 contains a summary of the bond distances and angles of the tetrazolium cation and Table 3 shows selected coordination geometry around the silver cations for the same three compounds. Lastly, Table 4 summarizes the geometry of the hydrogen-bonding for these compounds.

Table 1. Crystal structure solution and refinement for silver salts **9**, **11** and **13**

Parameter	9	11	13
empirical formula	C ₂ H ₆ N ₅ O _{4.5} ClAg	C ₂ H ₅ N ₅ O ₄ ClAg	C ₆ H ₁₅ N ₁₆ O ₃ Ag
formula weight [g mol ⁻¹]	315.44	306.43	467.21
temperature / K	100(2)	200(2)	200(2)
crystal size / mm	0.25×0.20×0.12	0.26×0.10×0.03	0.25×0.10×0.05
crystal system	Monoclinic	Monoclinic	Triclinic
space group	<i>C2/c</i>	<i>P2₁/c</i>	<i>P-1</i>
<i>a</i> / Å	13.303(2)	6.519(5)	7.179(1)
<i>b</i> / Å	11.616(2)	7.089(5)	11.380(1)
<i>c</i> / Å	12.019(2)	18.378(5)	11.440(1)
α / °	90	90	64.68(1)
β / °	111.93(1)	96.901(5)	79.00(1)
γ / °	90	90	79.87(1)
<i>V</i> _{UC} / Å ³	1723.0(4)	843.2(9)	824.6(1)
<i>Z</i>	8	4	2
ρ_{calc} / g cm ⁻³	2.432	2.414	1.882
<i>m</i> / mm ⁻¹	2.651	2.700	1.273
<i>F</i> (000)	1224	592	468
θ range / °	4.70-26.00	3.63-27.00	3.73-30.00
index ranges	-15 ≤ <i>h</i> ≤ 16 -14 ≤ <i>k</i> ≤ 13 -14 ≤ <i>l</i> ≤ 8	-8 ≤ <i>h</i> ≤ 8 -9 ≤ <i>k</i> ≤ 9 -23 ≤ <i>l</i> ≤ 23	-10 ≤ <i>h</i> ≤ 10 -16 ≤ <i>k</i> ≤ 16 -16 ≤ <i>l</i> ≤ 16
reflections collected	4342	6157	11037
independent reflections	1688 (<i>R</i> _{int} = 0.0729)	1829 (<i>R</i> _{int} = 0.0280)	4754 (<i>R</i> _{int} = 0.0414)
data/restraints/ parameters	1688/0/147	1829/0/138	4754/0/256
goodness-of-fit on <i>F</i> ²	1.016	1.157	0.822
<i>R</i> ₁ [<i>F</i> > 4σ(<i>F</i>)] ^[a]	0.0390	0.0292	0.0313
<i>R</i> ₁ (all data)	0.0543	0.0325	0.0540
w <i>R</i> ₂ [<i>F</i> > 4σ(<i>F</i>)] ^[b]	0.0877	0.0725	0.0609
w <i>R</i> ₂ (all data)	0.0966	0.0745	0.0756

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



Scheme 4. Labelling scheme for the 5-aminotetrazolium cation.

Table 2. Selected bond and angle geometries for silver salts **9**, **11** and **13**

Parameter	9	11	13 (A)	13 (B)	13 (C)
N5-C	1.338(6)	1.329(4)	1.335(3)	1.333(3)	1.338(3)
C-N1	1.344(7)	1.338(4)	1.333(3)	1.338(3)	1.335(3)
N1-N2	1.360(5)	1.335(4)	1.361(3)	1.357(3)	1.356(3)
N2-N3	1.295(7)	1.293(4)	1.285(3)	1.280(3)	1.278(3)
N3-N4	1.356(6)	1.334(4)	1.374(3)	1.363(3)	1.376(3)
N4-C	1.332(7)	1.352(4)	1.335(3)	1.329(3)	1.324(3)
N1-R ₁	1.452(9)		1.455(3)	1.449(3)	1.447(3)
N2-R ₂		1.465(5)			
N5-C-N1	124.1(4)	126.2(3)	125.7(2)	126.0(2)	125.9(2)
C-N1-N2	107.8(4)	102.7(2)	108.7(2)	108.3(2)	108.6(2)
N1-N2-N3	106.9(4)	114.1(3)	107.1(2)	107.0(2)	107.1(2)
N2-N3-N4	110.7(4)	106.0(3)	110.2(2)	110.6(2)	110.2(2)
N4-C-N5	106.1(4)	107.1(3)	126.3(2)	126.1(2)	126.1(2)
N4-C-N1	108.4(4)	110.2(2)	108.0(2)	107.9(2)	108.0(2)
R ₁ -N1-C	130.2(5)		130.5(2)	130.9(2)	130.1(2)
R ₁ -N1-N2	121.9(5)		120.6(2)	120.8(2)	121.2(2)
R ₂ -N2-N1		123.2(3)			
R ₂ -N2-N3		122.7(3)			

9: R₁ = NH₂, R₂ = CH₃; **11:** R₁ = NH₂, R₃ = CH₃; **13:** R₁ = NH₂, R₂ = CH₃.

Table 3. Selected coordination geometry around the silver cations in salts **9**, **11** and **13** (distances in Å and angles in °)

9			
Ag–N5	2.201(4)	Ag–N4	2.383(4)
Ag–N3	2.311(4)	Ag–O5	2.577(4)
N5–Ag–N3	134.3(1)	N5–Ag–O5	122.8(1)
N5–Ag–N4	121.1(1)	N3–Ag–O5	87.3(1)
N3–Ag–N4	94.1(1)	N4–Ag–O5	82.5(1)
11			
Ag–N2	2.171(3)	Ag–N5 ⁱⁱ	2.210(3)
Ag–O4 ⁱ	2.596(3)	Ag–O1 ⁱⁱⁱ	2.798(3)
Ag–O4 ⁱⁱ	2.816(3)		
N2–Ag–N5 ⁱⁱ	159.63(1)	N5 ⁱⁱ –Ag–O4 ⁱⁱ	81.3(1)
N2–Ag–O4 ⁱ	106.14(1)	N5 ⁱⁱ –Ag–O1 ⁱⁱⁱ	90.7(1)
N2–Ag–O4 ⁱⁱ	105.0(1)	O4 ⁱⁱ –Ag–O4 ⁱ	93.8(1)
N2–Ag–O1 ⁱⁱⁱ	83.1(1)	O4 ⁱⁱ –Ag–O1 ⁱⁱⁱ	171.8(1)
N5 ⁱⁱ –Ag–O4 ⁱ	92.55(1)	O1 ⁱⁱⁱ –Ag–O4 ⁱ	85.2(1)
13			
Ag–N5	2.186(2)	Ag–N15	2.201(2)
Ag–N10	2.184(2)		
N10–Ag–N5	122.1(1)	N5–Ag–N15	118.7(1)
N10–Ag–N15	118.8(1)		

Symmetry codes for **11**: (i) 1–x, 0.5+y, 1.5–z; (ii) 1+x, y, z; (iii) 1+x, 1+y, z.

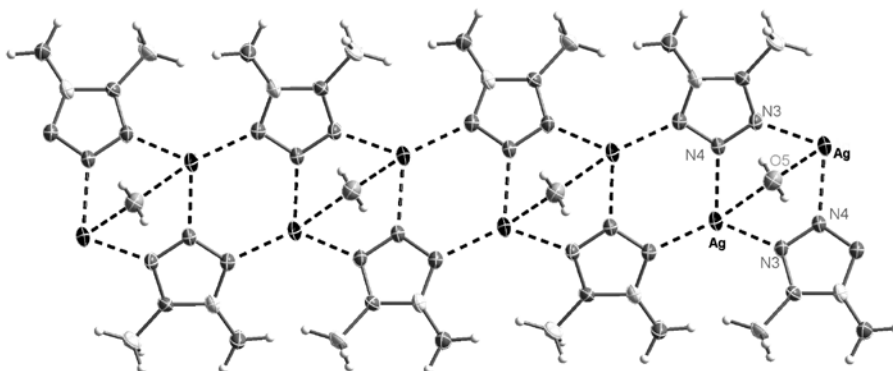
**Figure 3.** Heteronorbormane skeleton in the crystal structure of perchlorate salt **9**.

Table 4. Hydrogen-bonding geometry for the silver salts **9**, **11** and **13**

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
9				
N1–H1A...O3	0.90(6)	2.49(6)	3.360(7)	162(5)
O5–H5...O1	0.77(5)	2.43(6)	3.139(6)	154(6)
N1–H1B...O2 ^{iv}	0.94(6)	1.95(6)	2.871(7)	169(5)
N1–H1A...O2 ^v	0.90(6)	2.27(6)	3.011(7)	140(5)
11				
N1–H1A...O3 ⁱ	0.76(4)	2.23(4)	2.962(4)	161(4)
N1–H1B...O1 ⁱⁱⁱ	0.83(5)	2.32(5)	3.094(4)	157(5)
N1–H1B...O4 ⁱⁱⁱ	0.83(5)	2.62(5)	3.330(5)	145(5)
13				
N1–H35B...N14	0.74(3)	2.54(3)	3.284(3)	174(2)
N6–H33A...N4	0.77(3)	2.69(3)	3.445(3)	166(3)
N11–H31A...N9	0.79(3)	2.61(3)	3.374(3)	163(2)
N1–H35A...O1 ⁱ	0.88(3)	2.22(3)	3.086(3)	166(2)
N1–H35A...O2 ⁱ	0.88(3)	2.49(3)	3.184(3)	136(2)
N6–H33B...O2 ⁱⁱ	0.86(3)	2.21(3)	3.064(3)	171(3)
N6–H33B...O3 ⁱⁱ	0.86(3)	2.53(3)	3.200(3)	135(2)
N11–H31B...O3 ⁱⁱⁱ	0.87(3)	2.20(3)	3.066(3)	172(2)
N11–H31B...O1 ⁱⁱⁱ	0.87(3)	2.57(3)	3.224(3)	132(2)

9: (iv) 0.5–x, 1.5–y, –z; (v) 0.5+x, 1.5–y, 0.5+z. **11:** (i) 1–x, 0.5+y, 1.5–z; (iii) –x, 0.5+y, 1.5–z. **13:** (i) 2–x, 1–y, 1–z; (ii) 1–x, 2–y, 1–z; (iii) 1–x, 1–y, 2–z.

After recrystallization from water, compound **9** incorporates 0.5 molecules of water (i.e., $\mathbf{9} \cdot 0.5\text{H}_2\text{O}$) in the crystal structure. This half a molecule of water is crucial in determining the packing and makes for the formation of a heteronorbormane skeleton by coordination around the silver cations as depicted in Figure 3. This skeleton, which is the main building block of the structure is made out of two silver cations, four nitrogen atoms of the tetrazole ligands and an oxygen atom of a water molecule. The coordination around the silver cations in the structure is that of a distorted tetrahedron with three short distances in the range 2.2 to 2.4 Å and one longer contact to the water molecule of 2.577(4) Å. Lastly, the perchlorate anions are mere spectators and do not participate in the coordination around the silver cations.

Compound **12**, is the 2-methyl isomer of **9**. The absence of crystal water in the structure of the compound results in large differences in the packing. In particular, the coordination around the silver cations is no longer that of a distorted tetrahedron but rather that of a distorted square base pyramid (Figure 4) and is

formed by two short contacts to nitrogen atoms of ca. 2.2 Å and three longer ones to oxygen atoms in the range 2.6 to 2.8 Å. Note that here the perchlorate anions are not mere spectators as observed for compound **9** but they actually participate in the coordination around the silver cations.

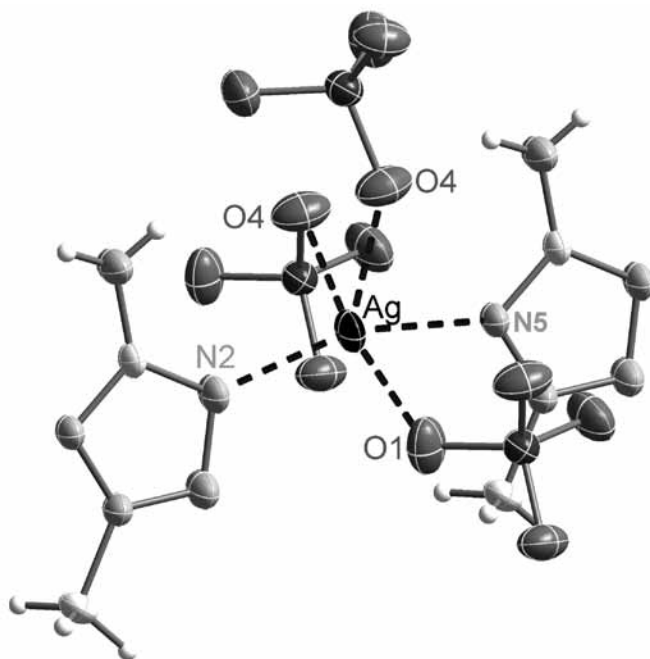


Figure 4. Coordination around the silver cations in perchlorate salt **11**.

As already pointed out above, recrystallization of nitrate salt **10** does not result in single crystals of this compound but in the formation of silver tris-(1-methyl-5-aminotetrazole) nitrate (**13**) as revealed by X-ray analysis (Figure 5). The helix-like coordination around the silver cations is completed by three short contacts in the range of ca. 2.2 Å, describing a slightly distorted *T*-shape geometry, with coordination angles very close to the expected 120°. As already observed for compound **9**, the nitrate anions do not participate in the coordination around the silver cations.

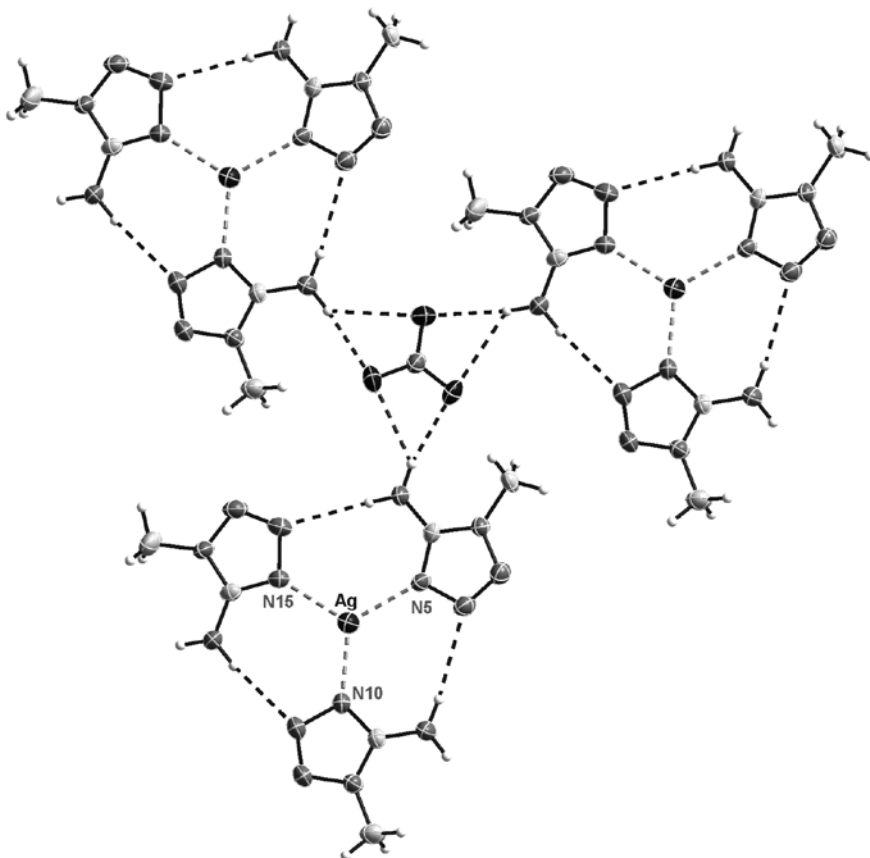


Figure 5. Coordination around the silver cations in nitrate salt **13**.

Table 5 shows a summary of the initial safety testing results for the silver salts in this study. All compounds in this study have high decomposition points (>225 °C). Only the 1-methyl-5-amino-1*H*-tetrazolium salts **9** and **10** have distinctive melting points, whereas the rest of the compounds either decompose without melting or, in the case of compound **11**, it melts with concomitant decomposition. The disilver derivatives **7** and **8** have high thermal stabilities above that of silver azide [18].

Table 5. Initial safety testing results for silver salts **7-12**

Compound ^[a]	Impact (J) ^[b]	Friction (N) ^[c]	ESD (+/-) ^[d]	T _m (°C) ^[e]	T _{dec} (°C) ^[f]	Thermal Shock ^[g]
7	2	<5	+	none	319	Explodes
8	15	18	+	none	298	Explodes
9	<5	120–360 ^[h]	–	154	252	Deflagrates
10	10	100–360 ^[h]	–	182	226	Deflagrates
12	2	<5	+	286	289	Deflagrates
13	20	100–360 ^[h]	–	none	259	Deflagrates

[a] Crystals of **9** (hemihydrate), **10** and **11** were used for the safety tests, whereas silver salts **7**, **8** and **12** were tested as powders; [b] Impact and [c] friction sensitivity (using standard BAM tests); [19–21] [d] Rough sensitivity to electrostatic discharge, + sensitive, – insensitive (using a Tesla coil); [e] melting point and [f] decomposition points (both from DSC measurements); [g] Response of the compound to fast heating using a *Bunsen* burner; [h] The compounds decompose non-explosively in this range.

In addition to DSC analysis, a small sample of the material was placed in the flame of a Bunsen burner to assess their response to thermal shock. In the case of the mono-silver based compounds **9-12** a deflagration was observed whereas the disilver salts **7** and **8** lead to loud explosions. In keeping with the sensitivities towards thermal shock, the trend in the impact and friction sensitivities seems to follow a similar trend, i.e., more sensitive compounds give a more vigorous response in the flame. In general terms, the perchlorate salts are much more sensitive towards impact and friction. However, it must be noticed that the crystalline state of the sample is of extreme importance when testing the sensitivity of energetic compounds, i.e., crystalline compounds tend to show higher sensitivities to impact and friction. In any case, the results initial safety results presented in this section are in good agreement with recent studies of the group on energetic nitrate and perchlorate salts [4, 5].

Conclusions

Convenient synthesis of novel silver nitrate and perchlorate salts with 5-aminotetrazole ligands is presented, which allow to obtain the compounds in good yields and purities. All compounds were characterized by analytical and spectroscopic methods and the X-ray structure of compounds **9**, **11** and **13** is presented here. In comparison to protonated tetrazolium salts **1-6** (see Scheme 1) the new compounds have higher thermal stabilities and are much more sensitive explosives. The trends in the sensitivities and thermal stabilities seems to correlate

well with the type of anion (perchlorate salts are more sensitive and have higher decomposition points than the analogous nitrate salts) and the type of ligand (salts with the 5-amino-1*H*-tetrazole ligand are more thermally stable than those containing the 2-methyl-5-amino-1*H*-tetrazole ligand, which are in turn more stable than those based on 1-methyl-5-amino-1*H*-tetrazole). Additionally, the disilver compounds (**7** and **8**) have higher decomposition temperatures and are much more sensitive than salts **9-12**, which contain only one silver cation. Finally, some of the materials described in this paper might hold promise for application as primary explosives to replace lead azide due to their lower sensitivities towards impact, friction and electrostatic discharge and their devoid of highly toxic lead.

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References

- [1] a) Fedoroff B.T., Sheffield O.E., *Encyclopedia of Explosives and Related Items*, Vol. 7, Dover NJ, Picatinny Arsenal, **1978**, I105; b) Huynh M.H.V., Hiskey M.A., Meyer T.J., Wetzler M., Green primaries: environmentally friendly energetic complexes, *Proc. Natl. Acad. Sci. U.S.A.*, **2006**, *103*, 5409-5412.
- [2] Huynh M.H.V., Coburn M.D., Meyer T.J., Wetzler M., Green Primary Explosives: 5-Nitrotetrazolato-N2-ferrate Hierarchies, *Proc. Natl. Acad. Sci. U.S.A.*, **2006**, *103*(27), 10322-10327.
- [3] Klapötke T.M., Miró Sabaté C., Welch J.M., Alkali Metal 5-Nitrotetrazolate Salts: Prospective Replacements for Service Lead(II)azide in Explosive Initiators, *Dalton*

- Trans.*, **2008**, 6372-6380.
- [4] Karaghiosoff K., Klapötke T.M., Mayer P., Miró Sabaté C., Penger A., Welch J.M., Salts of Methylated 5-Aminotetrazoles with Energetic Anions, *Inorg. Chem.*, **2008**, *47*, 1007-1019.
- [5] Klapötke T.M., Miró Sabaté C., Penger A., Rusan M., Welch J.M., Energetic Salts of Low Symmetry Methylated 5-Aminotetrazoles, *Eur. J. Inorg. Chem.*, **2009**, 880-896.
- [6] Smirnov A.V., Ilyushin M.A., Tselinsky I.V., *3rd Autumn Sem. Propell. Explos. Pyrotech.*, Chengdu, China, October 5th-8th, **1999**, 5-9.
- [7] a) Konkova T.S., Matyushin Y.N., Vorobev A., Sinditskii V.P., Dutov M.D., Fogelzang A.E., *36th Int. Ann. Conf. ICT – Energ. Mater.*, **2005**, *93*, 1-13; b) Konkova T.S., Matyushin Y.N., Vorobev A.B., Sinditskii V.P., Dutov M.D., *35th Int. Ann. Conf. ICT – Energ. Mater.*, **2004**, *96*, 1-13.
- [8] Zhou X., Jpn. Kokai Tokkyo Koho, JP 2000297078, **2000**.
- [9] a) Kizhnyaev V.N., Kruglova V.A., Complexation of Vinyltetrazoles and Their Polymers with Metal(II) Chlorides, *Zh. Prikl. Khim.*, **1992**, *65*, 1879-1884; b) Sorenson J.R.J., Copper Chelates as Possible Active Forms of the Antiarthritic Agents, *J. Med. Chem.*, **1976**, *19*, 135-148.
- [10] Henry R.A., Finnegan W.G., Lieber E., 1,4-Dialkyl-5-iminotetrazoles, *J. Am. Chem. Soc.*, **1954**, *76*, 2894-2898.
- [11] Rittenhouse C.T., *Bi-Silver Aminotetrazole Perchlorate*, US 3663553, **1972**.
- [12] a) Williamson K., Li P., Devlin J.P., Vibrational Spectra and Structures of Ionic Liquids. II. The Pure Alkali Metal Nitrates, *J. Chem. Phys.*, **1968**, *48*, 3891-3896; b) Fernandes J.R., Ganguly S., Rao C.N.R., Infrared Spectroscopic Study of the Phase Transitions in Cesium Nitrate, Rubidium Nitrate and Ammonium Nitrate, *Spectrochim. Acta A*, **1979**, *35*, 1013-1020.
- [13] a) Cohn H., Infrared Spectrum of Crystalline Potassium Perchlorate. Reassignment of the Lower Fundamental Frequencies of the Perchlorate Ion, *J. Chem. Soc.*, **1952**, 4282-4284; b) Redlich O., Holt E.K., Biegeleisen J., The Ionization of Strong Electrolytes. II. Ionizations, Raman Spectrum and Vibrations of HClO₄, *J. Am. Chem. Soc.*, **1944**, *66*, 13-16.
- [14] von Denffer M., Klapötke T.M., Kramer G., Spieß G., Welch J.M., Heeb G., Improved Synthesis and X-Ray Structure of 5-Aminotetrazolium Nitrate, *Propellants, Explos., Pyrotech.*, **2005**, *30*, 191-195.
- [15] Klapötke T.M., Miró Sabaté C., Stierstorfer J., Hydrogen-bonding Stabilization in Energetic Perchlorate Salts: 5-Amino-1*H*-tetrazolium Perchlorate and its Adduct with 5-Amino-1*H*-tetrazole, *Z. Anorg. Allg. Chem.*, **2008**, *11*, 1867-1874.
- [16] Sheldrick G.M., *Programs for Crystal Structure Analysis (Release 97- 2)*, University of Göttingen, Göttingen (Germany), **1998**.
- [17] Altomare A., Burla M. C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G, Spagna R., SIR97: a New Tool for Crystal Structure Determination and Refinement, *J. Appl. Crystallogr.*, **1999**, *32*, 115-119.
- [18] Köhler J., Meyer R., *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, Germany, **1998**.

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- [19] Impact: Insensitive > 40 J, less sensitive = 35 J, sensitive = 4 J, very sensitive = 3 J; friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a.> 80 N, very sensitive = 80 N, extremely sensitive = 10 N. According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates not safe for transport.
- [20] <http://www.bam.de>.
- [21] Klapötke T.M., Rienäcker C.M., Drophammer Test Investigations on Some Inorganic and Organic Azides, *Propellants, Explos., Pyrotech.*, **2001**, 26, 43-47.

