CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801666

Energetic Silver Salts with 5-Aminotetrazole Ligands

Konstantin Karaghiosoff, Thomas M. Klapötke,* and Carles Miró Sabaté[a]

Abstract: Methylation of 5-amino-1*H*-tetrazole (**1**) gives 1-methyl-5-amino-1*H*-tetrazole (**2**) and 2-methyl-5-amino-1*H*-tetrazole (**3**). A new family of energetic silver complexes based on ligands **1**, **2** and **3** with perchlorate and nitrate anions (**10**–**15**) were synthesized and characterized by using IR, Raman, and NMR (^{1}H, ^{13}C, ^{14}N, and ^{35}Cl NMR) spectroscopy, elemental analysis, and mass spectrometry. The crystal structures of the compounds were determined where possible and reveal interesting structural details that are discussed herein. Additionally, differential scanning calorimetry was used to assess the thermal stability of the new salts, which showed excellent thermal stabilities at temperatures up to and above 225 °C. Standard tests were also used to assess the sensitivity of the materials towards impact and friction. All the silver complexes showed increased sensitivity values in comparison with analogous protonated 5-amino-1*H*-tetrazolium perchlorate and nitrate salts. Some of these materials have sensitivity values that are comparable to commonly used primary explosives and all of them either deflagrate (**12**–**14**) or detonate loudly (**10** and **11**) on contact with an open flame. Lastly, nitrate salt **11** is easily initiated by thermal shock. It shows reasonably low sensitivity in comparison with other silver salts (e.g., silver azide or silver fulminate), which makes handling it much less hazardous. Compound **11** also has good thermal stability, decomposing at ≈300 °C, and shows interesting properties as a more environmentally benign alternative to lead(II) diazide in initiation devices for civil and military applications.

Keywords: energetic materials · heterocycles · silver · spectroscopic methods · X-ray diffraction

Introduction

Nitrogen-rich materials, and in particular tetrazoles, have great potential for energetic applications.[1–3] Tetrazole-based energetic materials[4] tend to have higher (more positive) heats of formation than analogous imidazoles or triazoles[4,5] and tend to have high thermal stabilities, regardless of their large positive enthalpies of formation.[6] Therefore, nitrogen-rich compounds based on, for example, nitrogen-rich 5-amino-1*H*-tetrazole (5-AT, **1**) are interesting in relation to the formation of endothermic (or less exothermic) compounds and environmentally friendly decomposition products.

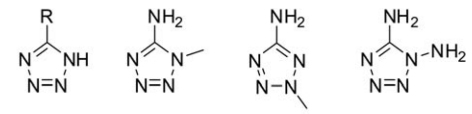
We recently reported the synthesis and characterization of salts of 5-AT with nitrate and perchlorate anions.[7,8] Methylation of 5-AT is known to give a mixture of 1-methyl- (1-MAT, **2**) and 2-methyl-5-amino-1*H*-tetrazole (2-MAT, **3**),[9] which can be separated by their different solubilities in water. We have also studied salts of these tetrazoles with nitric and perchloric acid as prospective insensitive energetic materials with reasonably high performances.[1g,2a] Because highly endothermic compounds often turn out to be very sensitive towards classical stimuli (i.e., friction and impact),[10] the introduction of small alkyl chains (i.e., methyl groups) helps to reduce the sensitivity of the material and at the same time increase its thermal stability at the cost of performance. Additionally, the introduction of methyl groups also makes interesting compounds accessible. For example, HN_3 is not able to protonate 5-AT to form the interesting azide salt; however, quaternization of the tetrazole allows the formation of different tetrazolium azide salts.[1g,2a]

The structure of some commonly used tetrazole-based ligands can be seen here. Most of the literature dealing with tetrazole-based materials concentrates on nitrogen-rich salts with cations such as ammonium,[11] hydrazinium,[11,12] guana-

---

[a] Prof. Dr. K. Karaghiosoff, Prof. Dr. T. M. Klapötke, Dr. C. Miró Sabaté
Department of Chemistry and Biochemistry
Energetic Materials Research
Ludwig-Maximilian University
Butenandstr. 5-13
81377, Munich (Germany)
Fax: (+49) 89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801666.



R = NH_2 (5-AT)
NO_2 (5-NT)

1-MAT

2-MAT

DAT

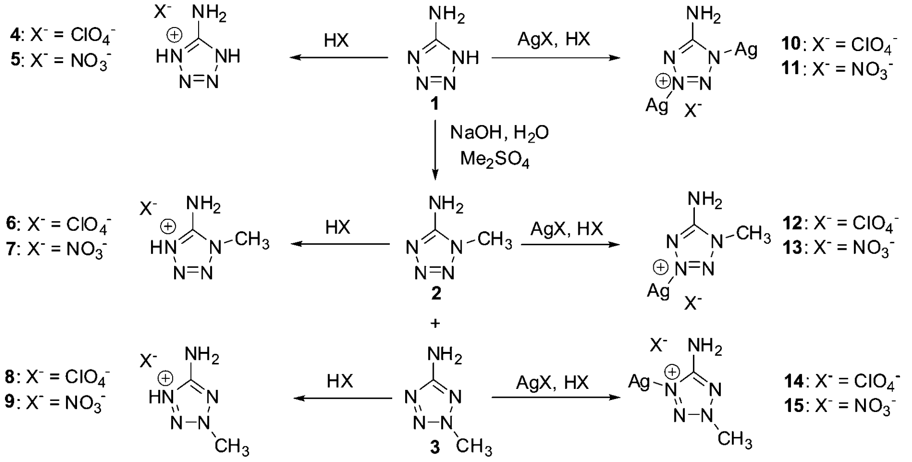
dinium,[11] aminoguanadinium,[11] diaminoguanidinium,[11] and triaminoguanidinium,[11,13] etc.,[14] or salts with energetic anions such as nitrate, perchlorate, picrate, azide, dinitramide,[15] 5,5′-azotetrazolate,[11a,12a,15] or 5-nitrotetrazolate,[3f,16] among others.[3f,17] On the other hand, descriptions of metal compounds that contain a tetrazole moiety are much more elusive in the literature and many of them are less interesting for use in energetic applications. Compounds of this type that have been reported before include 5-nitrotetrazole (5-NT) alkali salts of alkaline earth metals,[18] Fe^{2+},[19] $Co^{2+/3+}$,[20] Ni^{2+},[16] Cu^{2+},[21] and Hg^{+}[22]; salts of 1,5-diamino-1*H*-tetrazole (1,5-DAT) with Co^{3+},[23] Ni^{2+},[24a] Cu^{2+},[24] Zn^{2+}, and Cd^{2+};[24a] complexes of Mg^{2+} and Ca^{2+},[25a] Cr^{3+},[25b] $Fe^{2+/3+}$,[25b] $Co^{2+/3+}$,[25c,d] Ni^{2+},[25e] Cu^{2+},[25e,f] Zn^{2+},[25g] and Cd^{2+}[25h,i] with 5-AT; and 1R-substituted-5-AT transition-metal complexes of divalent and trivalent metals (Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, and Pd^{2+}) with R = Me (1-MAT),[26a] $CH_2C(=O)NH$-NH_2,[26b–d] $CH{=}CH_2$,[27a] and Ph.[27b] Some of these compounds have found uses in, or are prospective candidates for use in, pyrotechnic mixtures and they also have other interesting applications, such as their use in laser-induced explosives (LIEs; for example, Co complexes).[25d] LIEs are of interest for initiation because the wavelength of the incident light can be modulated so as to cause explosion of a compound that is insensitive to classical stimuli (i.e., shock and friction) and can thus be manipulated easily. However, the mechanism of induction is not well understood and magnetic measurements combined with crystal-structure analysis should help to explain this phenomenon, which is allegedly related to the excitation of electrons in d orbitals of transition metals. Unfortunately, apart from some recent work in our group on tetrazole-based alkali metal salts,[18a,28] some copper complexes,[1h,29a,c] and our last report on the molecular structure of silver 1-methyl-5-nitriminotetrazole,[29d] there are not many reports dealing with the crystal structure of tetrazole-based metal complexes, particularly when the cation is a transition metal. To our knowledge, the only examples reported so far are those of $[Ni(5\text{-}NT)_2]$,[16] $[Cd(5\text{-}AT)_2]$,[25i] $[CuCl_2(DAT)]$,[24b] and $[Co(1\text{-}MAT)_2(NH_3)_4]$.[23a]

Abstract in Spanish: *La metilación de 5-amino-1*H*-tetrazol (**1**) da lugar a la formación de 1-metil-5-amino-1*H*-tetrazol (**2**) y 2-metil-5-amino-1*H*-tetrazol (**3**). Una nueva familia de sales energéticas de plata con los ligandos **1**, **2** y **3** y con aniones perclorato y nitrato (**10–15**) fueron syntetizadas y caracterizadas mediante espectroscopías de IR, Raman y RMN (*^1H, ^{13}C, ^{14}N *y* ^{35}Cl*), analysis elemental y espectrometría de masas. La estructura cristalina de los compuestos fue medida cuando fue posible, mostrando detalles estructurales de interés que son discutidos. Adicionalmente, la estabilidad térmica de las nuevas sales fue medida utilizando calorimetría exploratoria diferencial, mostrando excelentes estabilidades térmicas por encima de los 225 °C. La sensibilidad de los materials al impacto y a la fricción fue también asesorada haciendo uso de tests estandarizados. Todos los complejos de plata son más sensibles a dichos estimulos que sales análogas conteniendo el anion perclorato o nitrato y cationes derivados de 5-amino-1*H*-tetrazol. Algunos de los materiales tienen sensibilidades que asemejan a compuestos explosivos primarios y todos ellos deflagran (**12–14**) o detonan fuertemente (**10** y **11**) cuando puestos en contacto con una llama. Finalmente, el nitrato **11** es fácil de iniciar a través de un choque térmico, tiene una sensibilidad razonablemente baja en comparación con otras sales de plata (p.ej., azida de plata o fulminato de plata) lo cual hace su uso menos peligroso, descompone a temperaturas elevadas (≈300 °C) y no contiene plomo(II) el cual es muy tóxico. Estas características lo hacen una alternativa más benigna para el medio ambiente para reemplazar la azida de plomo(II) en detonadores que se encuentran en aplicaciones tanto militares como civiles.*

In explosive devices, it is common to construct a so-called "explosive train",[30] which is typically made up of an initiator device and primary and secondary explosives. One of the problems of primary explosives is their low thermal stability. Silver salts tend to have high decomposition temperatures and are interesting for use as initiators (e.g., silver azide[31] or silver 5,5′-azotetrazolate[32]) due to the relatively benign character of silver (which is used in cutlery, for example) in comparison with commonly used initiators such as lead diazide ($Pb(N_3)_2$). In addition to heavy metal salts, (organic) perchlorate salts are also known to be rather sensitive compounds. In this context, disilver 5-amino-1*H*-tetrazolium perchlorate was patented as a new primary explosive with excellent thermal stability.[30] Therefore, we report herein the synthesis and full analytical, spectroscopic, and energetic characterization of silver salts with different 5-amino-1*H*-tetrazole ligands and perchlorate and (more environmentally benign) nitrate anions. These new compounds are analogous to our previously reported protonated tetrazolium salts and we compare the energetic properties of both sets of compounds. In addition, we report the crystal structures of four new silver salts with tetrazole-based ligands, which add to the few structural reports of azole-based metal salts and represent the first examples of silver salts with an azole ligand to have been structurally characterized.

Results and Discussion

Synthesis: To synthesize the silver–tetrazole complexes, disilver 5-amino-1*H*-tetrazolium perchlorate (**10**) was prepared by treating 5-AT with silver perchlorate in perchloric acid (Scheme 1) similarly to a previously reported procedure.[30] After the addition of water, the compound precipitated as a highly insoluble white powder that showed great sensitivity

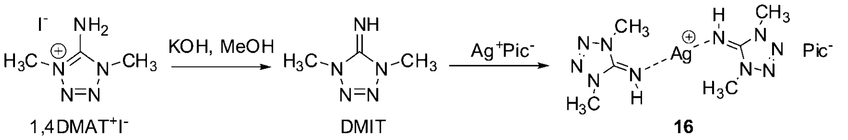


Scheme 1. Synthesis of the 5-aminotetrazolium nitrate and perchlorate salts.

towards shock and friction (primary explosive!). Primary explosives differ from secondary explosives in that they undergo a very rapid transition from burning to detonation and have the ability to transmit the detonation to a less sensitive explosive. Primary explosives will detonate when they are subjected to heat or shock. The interesting explosive properties of this compound prompted us to study other silver salts and we synthesized the nitrate derivative (**11**). To tune the high sensitivity of these compounds, 5-AT (**1**) was methylated by using dimethyl sulfate to give 1-MAT (**2**) and 2-MAT (**3**), which were treated either with silver nitrate or silver perchlorate in the corresponding acid (i.e., nitric or perchloric acid) to give a new family of silver salts with methylated tetrazole ligands (**12**–**15**).

Treatment of silver picrate (AgPic) with 1,4-dimethyl-5-amino-1*H*-tetrazolium iodide (1,4-DMAT$^+$I$^-$) to give the corresponding picrate salt[47c] also gave crystals of a byproduct that could be identified as bis-(1,4-dimethyl-5-imino-1*H*-tetrazole)silver picrate (**16**). Its formation can be explained by the method of preparation of AgPic from picric acid and KOH and subsequent metathesis with silver nitrate. Possibly unreacted KOH deprotonated the 1,4-DMAT$^+$ cation to form neutral 1,4-dimethyl-5-iminotetrazole (DMIT), which in turn reacted and coordinated with the silver picrate formed according to Scheme 2.

Lastly, an attempt at recrystallization to obtain crystals of **13** resulted in the formation of tris-(1-methyl-5-amino-1*H*-tetrazole)silver nitrate (**17**) and silver nitrate. The structure of this compound is discussed below.



Scheme 2. Reaction leading to the formation of **16**.

Vibrational and NMR spectroscopies: All silver salts were characterized by IR, Raman, and NMR spectroscopies where possible. The highly sensitive perchlorate and nitrate salts **10** and **11** are extremely insoluble in every common solvent, and only dissolve in concentrated acid solutions (e.g., hydrochloric, nitric, or perchloric acid) to form the corresponding 5-amino-1*H*-tetrazolium salt (chloride, nitrate, or perchlorate) in which the silver cations are no longer coordinating to the tetrazole ring; therefore, we omitted any NMR study on these two compounds.

The vibrational spectra show the characteristic bands of the respective energetic anions (nitrate and perchlorate) for each one of the compounds studied. In the nitrate salts, the anion shows a strong, broad IR absorption band centered at $\approx 1385\,\text{cm}^{-1}$ (see the Supporting Information, Figure S1) and a sharp strong band at $\approx 1040\,\text{cm}^{-1}$ ($1047\,\text{cm}^{-1}$ for **11**) in the Raman (see the Supporting Information, Figure S2).[33] For the silver salts, the perchlorate anion shows a strong stretching band with a maximum at 1085 to $1090\,\text{cm}^{-1}$ in the infrared spectra and strong, sharp bands at 925 to 930 and 460 to $465\,\text{cm}^{-1}$ in the Raman spectra.[34] These signals are in close agreement with those observed for our previously reported perchlorate and nitrate salts **4**[8] and **5**.[7]

Apart from the intense bands corresponding to the anion (see above), the IR and Raman spectra of the compounds also contain a set of bands that are characteristic for the cation. Two sharp, strong bands, with two smaller shoulders, at ≈ 3415 and $\approx 3325\,\text{cm}^{-1}$, which correspond to N–H stretching, were observed in the IR spectra of **10** and **11**. The rest of the compounds show a much more complicated set of bands in this region, with maxima at $\approx 3325\,\text{cm}^{-1}$ (**12** and **13**) and $\approx 3390\,\text{cm}^{-1}$ (**14** and **15**) in addition to C–H stretches between 2950 and $2860\,\text{cm}^{-1}$ in the case of the methylated compounds. After the anion stretch bands, the strongest absorption is the combined C=NH$_2$ stretching and NH$_2$ deformation modes found at $\approx 1620\,\text{cm}^{-1}$ in the IR spectra for **14** and **15** and which is shifted to $\approx 1635\,\text{cm}^{-1}$ for 2-MAT derivatives and as high as $\approx 1670\,\text{cm}^{-1}$ for 1-MAT derivatives in the methylated derivatives. This is in agreement with signals at higher energies ($\approx 1685\,\text{cm}^{-1}$) for protonated compounds **6** and **7**.[2a] Lastly, the rest of the bands are of lower intensity and can be assigned as follows: $\tilde{\nu} = 1550$–1350 (ν(tetrazole ring), δ_{as}(CH$_3$)), ≈ 1380 (δ(CH$_3$)), 1350–

700 (ν(N−C−N), ν(N−N), γ(CN), δ(tetrazole ring)), and $<700\,cm^{-1}$ (δout-of-plane bend (N−H), ω(NH_2)).[35]

IR spectroscopy also provides detailed insight into cation structure and interionic interactions, including hydrogen bonding.[36] A comparison of the IR spectra of the silver salts with those of 5-amino-1*H*-tetrazolium nitrate (**5**) and perchlorate (**4**) shows substantial changes, shifts, and sharpening of the $\tilde{\nu}$(N−H) bands observed in **4** and **5** if the ring protons are substituted by silver atoms. For example, perchlorate **4** shows two bands at 3437 and $3348\,cm^{-1}$,[8] which are shifted slightly lower to ≈3415 and $3326\,cm^{-1}$ (only one band at $\approx 3400\,cm^{-1}$ for the methylated derivatives) in the silver salts, which indicates a weakening (elongation) of the N−H bonds in the exocyclic amino group. In addition to providing information about hydrogen bonding and N−H bond strengths, the IR spectra also indicate other structural differences between silver salts (**10**–**15**) and their protonated analogues (**4**–**9**). For example, the IR spectra of **10** and **11** show strong bands at 1617 and $1620\,cm^{-1}$, respectively, that correspond to amino group deformation and also at 1557 and $1541\,cm^{-1}$, respectively, that correspond to C=N ring stretch.[37,38] In the spectra of **4** and **5**, a higher-energy band attributed to coupled amino group deformation and exocyclic C=N stretch is observed at $\approx 1700\,cm^{-1}$. This observation can be explained nicely by the structural changes expected on substitution of the ring protons by silver atoms, that is, the exocyclic $C{=}NH_2$ bond length should increase (decrease in stretching energy) as observed experimentally (see the X-ray discussion below).

As mentioned above, **10** and **11** were too insoluble to record an NMR spectrum in any solvent we tried. For the rest of the compounds, in the ^{1}H NMR spectra measured in [D_6]DMSO the protons of the amino group displayed resonances at $\delta \approx 6.0$ ppm for the 2-MAT derivatives and at $\delta \approx 7.0$ ppm for the 1-MAT derivatives. Both are strongly shifted to highfield in comparison with **4**[8] or **5**,[7] which is indicative of a decrease in the acidity of these protons in the silver complexes. The resonances of the methyl protons are found at $\delta \approx 3.7$ and ≈4.0 ppm for the 1-MAT derivatives and the 2-MAT derivatives, respectively. In the ^{13}C NMR spectrum the signals of the 1-MAT derivatives are shifted to highfield with respect to those of the 2-MAT derivatives (as also observed in the ^{1}H NMR spectrum). The shifts of the methyl group and the ring carbon atom are observed at $\delta \approx 32.0$ and ≈39.0 ppm and at $\delta \approx 156.0$ and ≈167.0 ppm ($\delta \approx 152.0$ ppm for **4**),[8] respectively. The ^{14}N NMR spectra clearly show only the resonance of the anion in the nitrate salts at $\delta \approx -4$ ppm (see the Supporting Information, Figure S3). In comparison with the protonated species, silver salts **12**–**15** tend to show ^{1}H and ^{13}C resonances that are shifted to higher field.[2a]

Crystal structures: Compounds **10**, **11**, and **15** always formed as powders upon recrystallization from several solvents, and **13** formed as a microcrystalline powder and rearranged to form **17** after recrystallization from water. Therefore, any structural characterization of these compounds was not possible and is in consequence omitted from this work. Crystals were obtained for the rest of the compounds as described in the Experimental Section. 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 $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). 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.[39,40] All hydrogen atoms were located by using difference Fourier electron-density maps, except for **17** in which the hydrogen atoms were placed at idealized positions. For all structures, all hydrogen atoms were refined isotropically. Crystallographic data are summarized in Table 1, selected bond lengths and angles are reported in Table 2, and the geometry around the Ag^+ cations can be found in Table 3. Additionally, hydrogen-bonding geometries and the results of the graph set analysis are available in the Supporting Information Tables S1–5. CCDC-693944 (**12**), -693945 (**14**), -693946 (**16**), and -693947 (**17**) 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

Compound **12** crystallizes with half a molecule of water of crystallization in a monoclinic unit cell (space group *C*2/*c*) with $Z = 8$. The coordination around the Ag^+ cation is depicted in Figure 1a and is composed of short interactions of between ≈2.2 and 2.4 Å to each one of the nonsubstituted ring nitrogen atoms (N3, N4, and N5) and a longer contact to the water molecule at 2.577(4) Å (3+1). The distances and angles around the cation agree with those of the rest of the silver salts in this and other studies.[41]

The role of the water molecules in the structure is crucial in determining the packing. Figure 2 shows the heteronorbornane skeleton, which is the main building block of the structure. This is made from two Ag^+ cations, two times two nitrogen atoms that correspond to two crystallographically related 1-MAT ligands, and the long contact to O5 of a water molecule (described above), which coordinate two contiguous cations. In addition, the third (nonsubstituted) nitrogen atom in the tetrazole ring (N5) connects the heteronorbornane units with the shortest contact found in the structure (Ag···N5 = 2.201(5) Å) and forms infinite chains through the crystal along a direction that is approximately parallel to the *c* axis. The chains, which are positively charged due to the Ag^+ cations, are separated from the perchlorate anions.

See Figure 3 for a representative view of a super cell of the crystal structure of **12** that shows the loose (noncoordinating) perchlorate anions and a front view of the structure skeleton along the *c* axis with the norbornane moieties crossing each other and sharing a common point placed ≈3.7 Å for the water molecules. The computer program RPLUTO[42,43] identifies the four hydrogen bonds summarized in Table S1 (Supporting Information) as forming a primary graph set of the type $N_1 = \mathbf{DDDD}$, in which one of the dimeric units ($\mathbf{D} = \mathbf{D}_1^1\mathbf{(2)}$) is involved in the formation of a larger finite pattern with the label **$D_2^2(5)$** (see the Supporting Information, Table S2). At the secondary level, many other dimeric **$D_2^2(5)$** graph sets are found together with ring motifs. Graph sets of the type **$R_1^2(4)$** are formed between one of the hydrogen atoms of the amino group and two oxygen atoms of the anion (Figure 1b), whereas the larger **$R_4^2(8)$** and **$R_4^4(12)$** motifs are formed by the interaction of two anions and two cations without including and including the chlorine atoms labeled as Cl and Cl^{vi}, respectively (symmetry code: vi: $-x$, y, $-0.5-z$).

Figure 4a shows a view of the asymmetric unit of perchlorate **14**. This, in contrast to **12**, crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ but with a very similar crystal density ($\approx 2.4\ g\,cm^{-3}$). The lack of water of crystallization influences the packing strongly. To start with, all atoms in the ligand are crystallographically independent, whereas there are two types of crystallographically related nitrogen atoms in the 1-MAT ligand in **12**. More notable is the type of coordination observed around the Ag^+ cations in **14** (Figure 4b), which in this case can be described as 2+3 with $\sphericalangle N2\text{-}Ag\text{-}N5^{ii} = 159.6(1)°$ (symmetry code: ii: $1+x$, y, z) formed by two short contacts to tetrazole nitrogen atoms ($Ag \cdots N \approx 2.2$ Å) and three longer ones to perchlorate anions in the range of ≈ 2.6 to ≈ 2.8 Å (see Table 3), whereas in **12** the Ag^+ cations and perchlorate anions were isolated from each other.

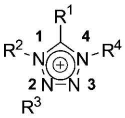
A view of the unit cell in the structure of the compound is depicted in Figure 5, in which the 2-MAT ligands interact with Ag^+ cations to form infinite chains along the a axis and the perchlorate anions intervene in the formation of inter-

Table 1. Crystal structure solution and refinement for silver–tetrazole complexes.

	12	**14**	**16**	**17**
empirical formula	$C_2H_6N_5O_{4.5}ClAg$	$C_2H_5N_5O_4ClAg$	$C_{12}H_{16}N_{13}O_7Ag$	$C_6H_{15}N_{16}O_3Ag$
M_r	315.44	306.43	562.25	467.21
T [K]	100(2)	200(2)	200(2)	200(2)
crystal size [mm]	0.25×0.20×0.12	0.26×0.10×0.03	0.35×0.10×0.08	0.25×0.10×0.05
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.303(2)	6.519(5)	7.233(5)	7.179(1)
b [Å]	11.616(2)	7.089(5)	14.260(5)	11.380(1)
c [Å]	12.019(2)	18.378(5)	20.874(5)	11.440(1)
α [°]	90	90	72.467(6)	64.68(1)
β [°]	111.93(1)	96.901(5)	83.214(5)	79.00(1)
γ [°]	90	90	81.500(5)	79.87(1)
V_{UC} [Å^3]	1723.0(4)	843.2(9)	2024.2(2)	824.6(1)
Z	8	4	4	2
ρ_{calc} [$g\,cm^{-3}$]	2.432	2.414	1.845	1.882
μ [mm^{-1}]	2.651	2.700	1.065	1.273
$F(000)$	1224	592	1128	468
θ range [°]	4.70–26.00	3.63–27.00	3.80–27.00	3.73–30.00
index ranges	$-15 \le h \le 16$ $-14 \le k \le 13$ $-14 \le l \le 8$	$-8 \le h \le 8$ $-9 \le k \le 9$ $-23 \le l \le 23$	$-9 \le h \le 9$ $-18 \le k \le 18$ $-26 \le l \le 26$	$-10 \le h \le 10$ $-16 \le k \le 16$ $-16 \le l \le 16$
reflns collected	4342	6157	22441	11037
indep. reflns	1688 (R_{int}=0.0729)	1829 (R_{int}=0.0280)	8806 (R_{int}=0.0688)	4754 (R_{int}=0.0414)
data/restraints/params	1688/0/147	1829/0/138	8806/0/611	4754/0/256
GOF on F^2	1.016	1.157	1.005	0.822
R_1 [$F > 4\sigma(F)$][a]	0.0390	0.0292	0.0533	0.0313
R_1 (all data)	0.0543	0.0325	0.0997	0.0540
wR_2 [$F > 4\sigma(F)$][b]	0.0877	0.0725	0.1057	0.0609
wR_2 (all data)	0.0966	0.0745	0.1213	0.0756

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

Table 2. Selected bond [Å] and angle [°] geometries for silver–tetrazole complexes.[a]



	12	**14**	**16(A)**[b]	**16(B)**[b]	**17(A)**[c]	**17(B)**[c]	**17(C)**[c]
R^1–C	1.338(6)	1.329(4)	1.286(1)	1.273(1)	1.335(3)	1.333(3)	1.338(3)
C–N1	1.344(7)	1.338(4)	1.374(1)	1.358(1)	1.333(3)	1.338(3)	1.335(3)
N1–N2	1.360(5)	1.335(4)	1.371(1)	1.351(1)	1.361(3)	1.357(3)	1.356(3)
N2–N3	1.295(7)	1.293(4)	1.263(1)	1.282(1)	1.285(3)	1.280(3)	1.278(3)
N3–N4	1.356(6)	1.334(4)	1.362(1)	1.360(1)	1.374(3)	1.363(3)	1.376(3)
N4–C	1.332(7)	1.352(4)	1.354(1)	1.360(1)	1.335(3)	1.329(3)	1.324(3)
N1–R^2	1.452(9)		1.447(1)	1.452(1)	1.455(3)	1.449(3)	1.447(3)
N2–R^3		1.465(5)		1.457(1)			
N4–R^4			1.462(1)				
R^1-C-N1	124.1(4)	126.2(3)	126.6(1)	127.4(1)	125.7(2)	126.0(2)	125.9(2)
C-N1-N2	107.8(4)	102.7(2)	109.4(1)	111.5(1)	108.7(2)	108.3(2)	108.6(2)
N1-N2-N3	106.9(4)	114.1(3)	109.0(1)	107.7(2)	107.1(2)	107.0(2)	107.1(2)
N2-N3-N4	110.7(4)	106.0(3)	107.9(1)	108.0(1)	110.2(2)	110.6(2)	110.2(2)
N4-C-R^1	106.1(4)	107.1(3)	111.2(1)	110.7(1)	126.3(2)	126.1(2)	126.1(2)
N4-C-N1	108.4(4)	110.2(2)	102.6(1)	102.1(1)	108.0(2)	107.9(2)	108.0(2)
R^2-N1-C	130.2(5)		128.4(2)	130.5(2)	130.5(2)	130.9(2)	130.1(2)
R^2-N1-N2	121.9(5)		122.2(2)	120.1(2)	120.6(2)	120.8(2)	121.2(2)
R^3-N2-N1		123.2(3)					
R^3-N2-N3		122.7(3)					
R^4-N4-N3			127.2(1)	129.1(2)			
R^4-N4-C			121.6(1)	120.2(1)			

[a] **12**: $R^1 = NH_2$, $R^2 = CH_3$; **14**: $R^1 = NH_2$, $R^3 = CH_3$; **16**: $R^1 = NH$, $R^2 = R^4 = CH_3$; **17**: $R^1 = NH_2$, $R^2 = CH_3$. [b] **A** and **B** refer to the two asymmetric units of **16** in the crystal structure. [c] **A**, **B**, and **C** refer to the three asymmetric units of **17** in the crystal structure.

Table 3. Selected bond [Å] and angle [°] coordination geometries around the Ag^+ cations in **12**, **14**, **16**, and **17**.

12		**14**[a]		**16**		**17**	
Ag–N5	2.201(4)	Ag–N2	2.171(3)	Ag1–N1	2.088(4)	Ag–N5	2.186(2)
Ag–N3	2.311(4)	Ag–O4^{i}	2.596(3)	Ag1–N16	2.092(5)	Ag–N10	2.184(2)
Ag–N4	2.383(4)	Ag–O4^{ii}	2.816(3)	Ag2–N6	2.097(5)	Ag–N15	2.201(2)
Ag–O5	2.577(4)	Ag–N5^{ii}	2.210(3)	Ag2–N11	2.109(4)		
		Ag–O1^{iii}	2.798(3)				
N5-Ag-N3	134.3(1)	N2-Ag-N5^{ii}	159.63(1)	N1-Ag1-N16	176.4(2)	N10-Ag-N5	122.1(1)
N5-Ag-N4	121.1(1)	N2-Ag-O4^{i}	106.14(1)	N6-Ag2-N11	169.3(2)	N10-Ag-N15	118.8(1)
N3-Ag-N4	94.1(1)	N2-Ag-O4^{ii}	105.0(1)			N5-Ag-N15	118.7(1)
N5-Ag-O5	122.8(1)	N2-Ag-O1^{iii}	83.1(1)				
N3-Ag-O5	87.3(1)	N5^{ii}-Ag-O4^{i}	92.55(1)				
N4-Ag-O5	82.5(1)	N5^{ii}-Ag-O4^{ii}	81.3(1)				
		N5^{ii}-Ag-O1^{iii}	90.7(1)				
		O4^{ii}-Ag-O4^{i}	93.8(1)				
		O4^{ii}-Ag-O1^{iii}	171.8(1)				
		O1^{iii}-Ag-O4^{i}	85.2(1)				

[a] Symmetry codes for **14**: i: $1-x$, $0.5+y$, $1.5-z$; ii: $1+x$, y, z; iii: $1+x$, $1+y$, z.

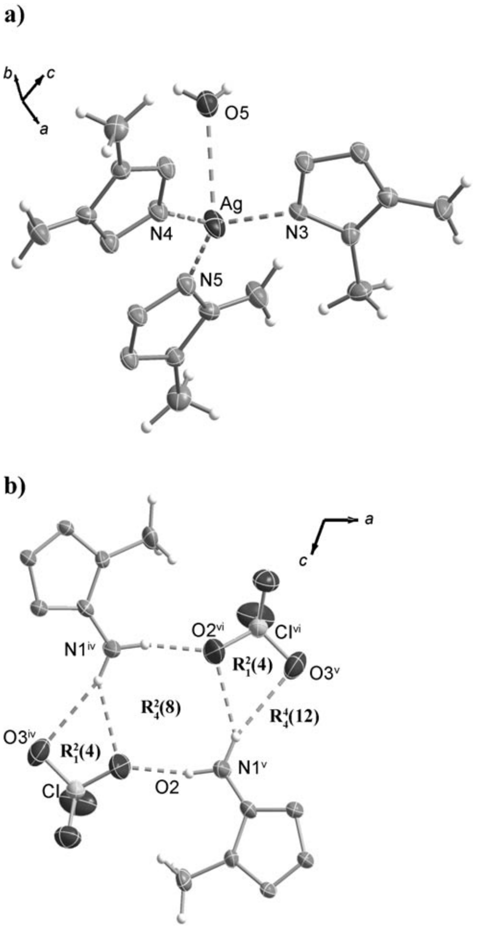


Figure 1. a) Full coordination around the Ag^+ cations and b) ring graph sets of interest in the crystal structure of **12** (view along the *b* axis) (symmetry codes: iv: $-0.5+x$, $1.5-y$, $-0.5+z$; v: $0.5-x$, $1.5-y$, $-z$; vi: $-x$, y, $-0.5-z$).

chain interactions to the cations. Lastly, the graph set analysis of **14**, which only forms three hydrogen bonds, is straightforward. The three finite chains found at the primary level (Table S3), combine to form a $\mathbf{R_1^2(4)}$ graph set, similar to that found in **12**, and two $\mathbf{C_2^2(6)}$ chain motifs.

16 was obtained as yellow needlelike crystals and forms a triclinic unit cell (space group $P\bar{1}$), with a significantly low calculated density in comparison to the perchlorate salts reported above ($1.845\ g\,cm^{-3}$). Figure 6 shows a view of the asymmetric unit of the compound. There exists two types of crystallographically independent and noninteracting **16**

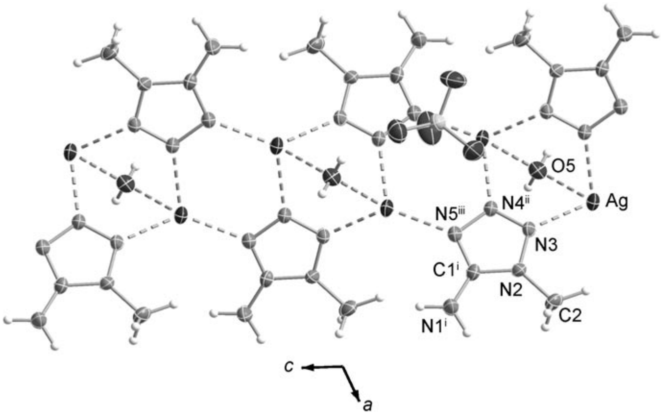


Figure 2. Heteronorbornane skeleton formed by the coordination of water molecules to the Ag^+ cations (dotted lines) in the crystal structure of **12**, with labeling system (symmetry codes: i: x, $1-y$, $0.5+z$; ii: $-x$, y, $0.5-z$; iii: x, $1-y$, $0.5+z$).

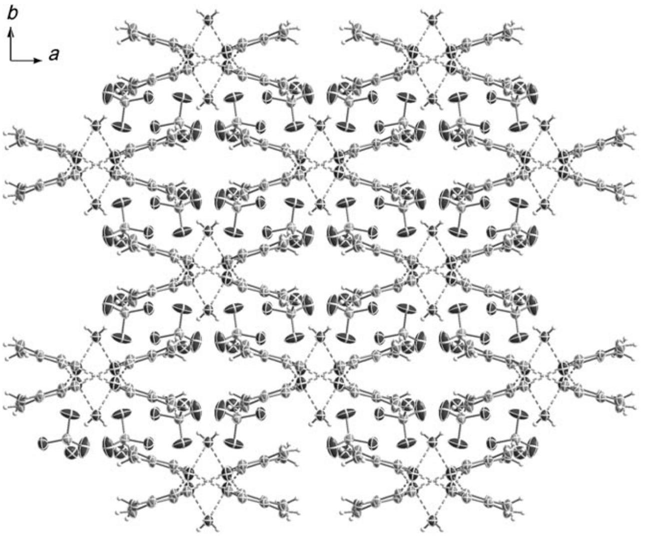


Figure 3. View of a supercell along the *c* axis in the crystal structure of **12**.

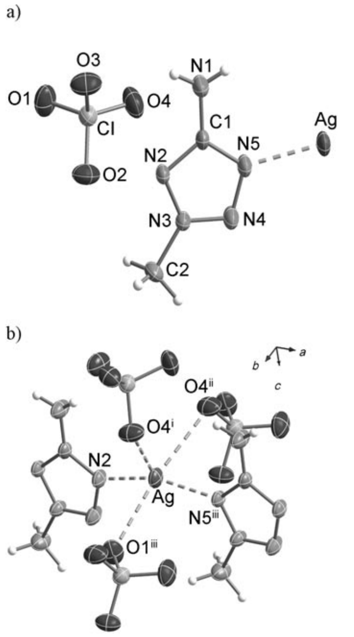


Figure 4. a) Asymmetric unit of **14** showing the labeling system. b) Coordination around the Ag^+ cations in the crystal structure of **14** (symmetry codes: i: 1−*x*, 0.5+*y*, 1.5−*z*; ii: 1+*x*, *y*, *z*; iii: 1+*x*, 1+*y*, *z*).

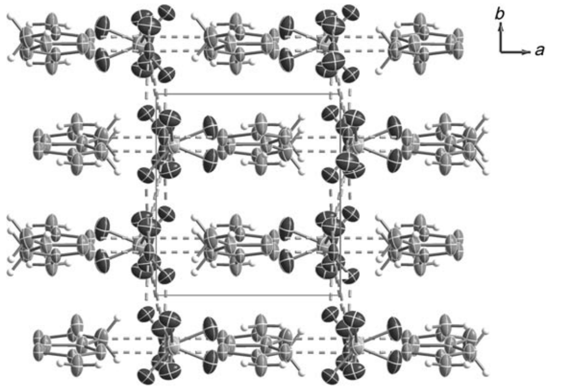


Figure 5. View of the unit cell along the *c* axis showing the formation of chains along the *a* axis in the crystal structure of **14**.

moieties, both of which show the simple linear coordination expected for the Ag^+ cations, similar to salts with the $[Ag(NH_3)_2]^+$ cation,[45a] with $\sphericalangle$N-Ag-N = 169.2(1) and 176.4(1)° presenting a distorted linear geometry.

The hydrogen atoms of the imino group interact with the picrate anions to form a total of three hydrogen bonds (see the Supporting Information, Table S1) with distances between donor (N) and acceptor (O) varying between ≈3.0 and 3.2 Å. In addition to classical hydrogen bonds, strong non-classical interactions exist between C3 and O7 and O8 with distances of 3.263(2) and 3.282(2) Å, respectively, which is similar to the sum of the van der Waals radii ($r_C + r_O$ = 3.26 Å),[46] and is common for picrate salts. Figure 7 shows a view of the unit cell of the compound along the *a* axis. The $[Ag(DMIT)_2]^+$ moieties form interrupted chains approximately parallel to the *b* axis by interacting(through the hydrogen bonds described above) with anions, which are placed at the vertices of the unit cell and in the center giving rise to π stacking. The formation of up to six different hydrogen bonds in the structure of the compound yields only finite chains at the unitary level (Supporting Information, Table S4), as noted for the rest of the compounds. At the secondary level, only some of them combine to form a small $\mathbf{D}_2^1\mathbf{(3)}$ and two larger $\mathbf{D}_2^2\boldsymbol{(X)}$ (X = 7, 9) graph sets. Lastly, the formation of several $\mathbf{R}_1^2\mathbf{(6)}$ graph sets by the interaction of the phenolate oxygen atom and one of the oxygen atoms of a nitro group at the *ortho* position with the imino moiety (NH) is common for azolium picrates.[47]

In contrast with perchlorate salt **12**, recrystallization of **13** from water results in rearrangement of the coordination sphere around the Ag^+ cations and more ligands than expected (i.e., three) are found to coordinate the metal. This

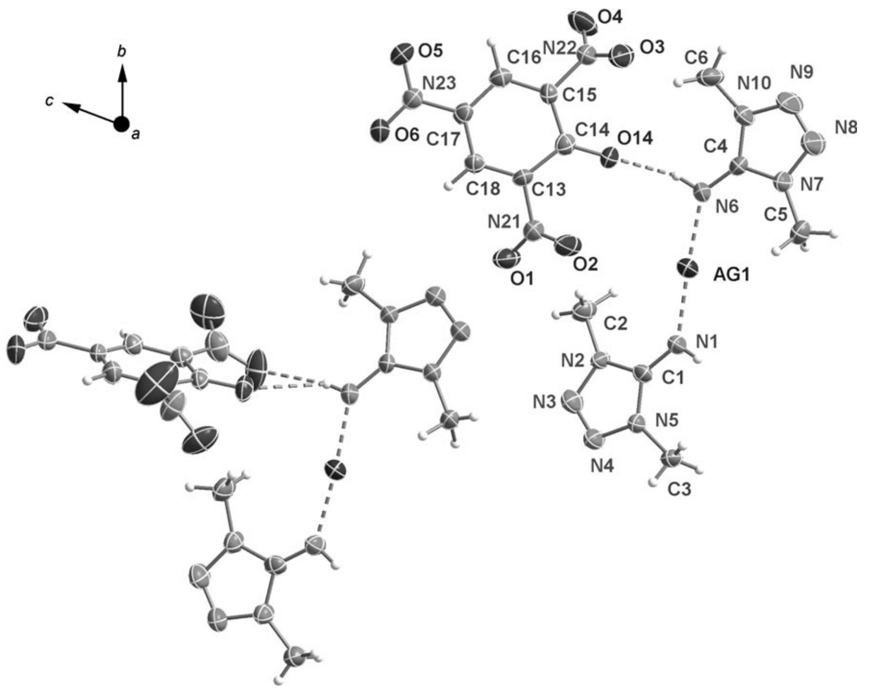


Figure 6. View of the asymmetric unit of **16** showing the coordination to the Ag^+ cations and the hydrogen bonding to the picrate anion, with the labeling system. Only half of the asymmetric unit has been labeled for clarity reasons.

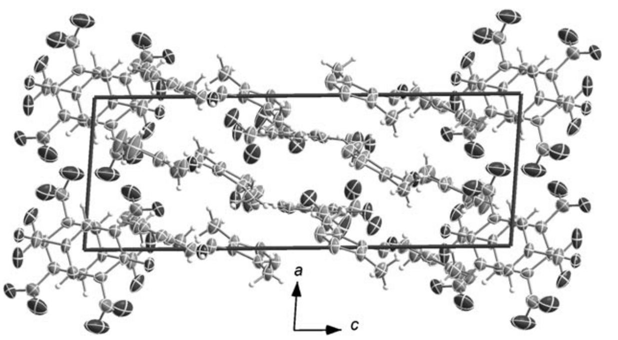


Figure 7. View of the unit cell of **16** along the *b* axis showing the stacks of anions in this direction.

results in a lower density compared with the perchlorate salts in this report ($1.882\,\mathrm{g\,cm^{-3}}$). As represented in Figure 8, the Ag^+ cations are surrounded by three 1-MAT ligands to form a slightly distorted T-shape geometry, so the coordination number in **17** is three. The coordination distances and angles are summarized in Table 3. All three distances are very similar (≈ 2.2 Å) and comparable to the Ag–N distances in the other complexes described here. On the other hand, the angles vary little from the ideal angle of 120°. The nitrate anions do not participate in the coordination sphere, but sit on a plane above and with a staggered configuration with respect to the coordination of the Ag^+ cations. The nearest oxygen atom in the anion is placed further away from the metal center than the sum of the van der Waals radii (Ag–O1 = 3.359(2) Å).[46]

It is interesting to note that the coplanarity of all cations, anions, and ligands (excepting the hydrogen atoms) results in the coordinating 1-MAT ligands sitting on the same plane and these are in turn linked to each other by weak hydrogen bonds in the range of 3.25 to 3.45 Å. This results in the formation of almost perfect layers along a direction that cuts all (*a*, *b*, and *c*) axes at an angle of $\approx 45°$. Figure 9 shows the hydrogen bonding in one of these layers, in which the $[Ag(1\text{-}MAT)_3]^+$ units described above are connected to each other through weak hydrogen bonds in the range of 3.05 to 3.25 Å to nitrate anions. These hydrogen bonds describe several graph sets of interest, which are identical for all three ligands and are summarized for one of them in Table S5 in the Supporting Information. As well as the usual dimeric interactions ($\mathbf{D}_1^1(2)$, $\mathbf{D}_2^1(3)$, and $\mathbf{D}_2^2(5)$), it is worth noting the formation of $\mathbf{R}_1^2(4)$ hydrogen-bonding networks between the nitrogen atoms of the amino groups (donors) and the oxygen atoms in the anions (acceptors). We found this motif to be common for other ionic compounds that contain an $-NO_2$ moiety, such as dinitramide ($-N(NO_2)_2$) and other nitrate salts,[2a,44] and also for the perchlorate salts (i.e., $-ClO_2$) discussed above.

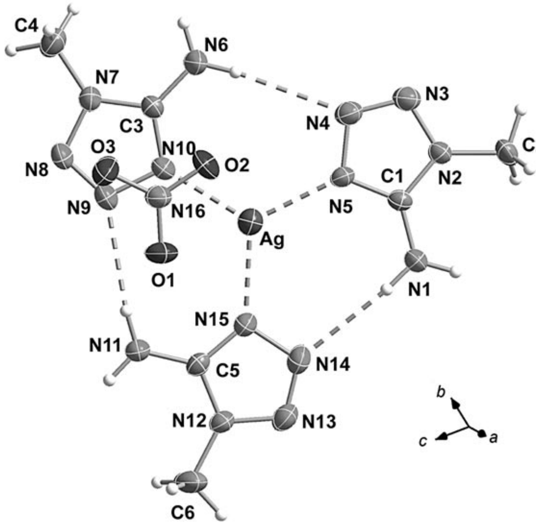


Figure 8. View of the asymmetric unit of **17** showing the coordination to the Ag^+ cations and the hydrogen bonding between the 1-MAT ligands, with the labeling system.

Energetic properties: To assess the energetic properties of all materials, we experimentally determined the thermal stability (differential scanning calorimetry (DSC) measurement onsets) and sensitivity to impact, friction,[48–50] electrostatic discharge, and thermal shock for each compound. The results of these studies are summarized in Table 4.

DSC studies on small samples of the energetic silver salts show excellent thermal stabilities above 225 °C. The 1-MAT derivatives additionally show distinctive melting points (154 °C for **12** and 182 °C for **13**) and the loss of the half-molecule of water of crystallization in **12** is shown as a broad endothermic peak at 102 °C, close to the boiling point of water. **14** shows a small melting endotherm (286 °C) shortly before decomposing at 289 °C, whereas **15** decomposes without melting at 259 °C. The disilver salts **10** and **11** (see Figure 10) have surprisingly high thermal stabilities according to DSC measurements (higher than the rest of the compounds in this study) and decompose at 319 and 298 °C, respectively, (also without melting) so that the trend in the decomposition points correlates well with the type of tetrazole ligand involved and increases in the order 1-MAT < 2-MAT < 5-AT. To summarize, the replacement of the ring hydrogen atoms in compounds **4**–**9** to form the corresponding silver salts (**10**–**15**) increases the melting and decomposition points considerably. Additionally, perchlorate-anion-based salts show larger liquid ranges among the compounds that melt and higher decomposition temperatures than the parent nitrate salts for all cases. Lastly, the decomposition (and melting) points are in keeping with known heterocycle-based salts[2a,51] and are comparable to the commonly used (but highly toxic) primary explosive lead diazide ($Pb(N_3)_2$).[52]

In addition to DSC analysis, the response of each compound to fast thermal shock was tested by placing a small sample of the material in a flame. Again, trends can be established for perchlorate and nitrate salts. In general, the perchlorate salts were more sensitive to fast heating than the corresponding nitrates. For example, in this study the four perchlorates, **4**, **6**, **8**, and **10**, exploded in the flame,

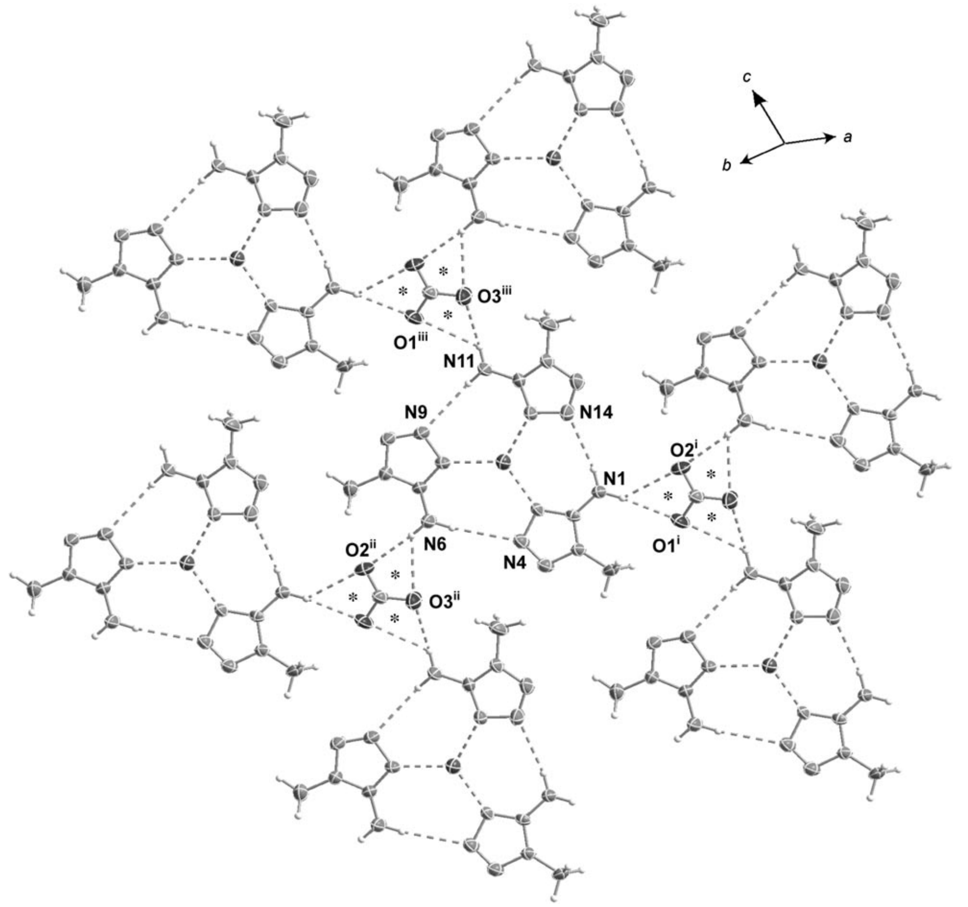


Figure 9. Hydrogen bonding and coordination around the Ag^+ cations in a layer of the crystal structure of **17** (symmetry codes: i: $2-x$, $1-y$, $1-z$; ii: $1-x$, $2-y$, $1-z$; iii: $1-x$, $1-y$, $2-z$). Graph set for rings marked *: $\mathbf{R_1^2(4)}$.

Table 4. Comparison of initial safety testing results for silver complexes and tetrazolium salts.[a]

	Impact [J]	Friction [N]	ESD (+/−)[b]	T_m[c] [°C]	T_{decomp}[d] [°C]	Thermal shock
4[e]	1.5	8	+	176	180	explodes
5[f]	>30	>360	−	none	173	deflagrates
6[g]	3	10	+	125	245	explodes
7[g]	>30	>360	−	162	178	burns
8[h]	1	6	+	125	196	explodes
9[h]	>30	>360	−	123	161	burns
10	2	<5	+	none	319	explodes
11	15	18	+	none	298	explodes
12	<5	120–360[i]	−	102 ($-H_2O$), 154	252	deflagrates
13	10	100–360[i]	−	182	226	deflagrates
14	2	<5	+	286	289	deflagrates
15	20	100–360[i]	−	none	259	deflagrates

[a] Compounds **4**, **5**, **6**–**9**, **12** (hemihydrate), **13**, and **14** were tested as the crystalline compounds; compounds **10**, **11**, and **15** were tested as powders; [b] Rough sensitivity to electrostatic discharge, +: sensitive, −: insensitive (using a Tesla coil); [c] Melting or temperature of water loss (**12**) and [d] decomposition points (from DSC measurements); [e] From ref. [8]; [f] From ref. [7]; [g] From ref. [2a]; [h] From ref. [44]; [i] The compounds decompose nonexplosively in this range.

whereas the analogous nitrate salts (**5**, **7**, **9**, and **11**) either burned or deflagrated. In addition, the disilver salts (**10** and **11**) are more reactive (both exploded) than the monosilver salts (**12**–**15**), which deflagrated in the "flame test".

Data collected for impact, friction, and electrostatic discharge sensitivities are also summarized in Table 4. The trend in the sensitivity values reflects that found in the response to fast heating, that is, the more sensitive the compound, the more vigorously it reacted in the flame test. In general, the perchlorate salts are very sensitive towards both friction and impact. For example, **4** is a very impact- and friction-sensitive compound (1.5 J and 8 N) and introduction of a methyl group to form **6** or **8** would be expected to result in lower sensitivity. However, it must be taken into consideration that there are many other factors that play a role in determining the sensitivity properties of energetic materials.

One factor that plays a major role in determining the friction and shock sensitivity of a compound is its crystallinity and the shape of the crystals. Compounds **4**, **6**, and **8** were tested as crystalline compounds; however, compounds **6** and **8** precipitate as large thick crystals whereas **4** forms as very thin platelets. This would explain the unexpectedly high friction and shock values for the two methylated perchlorate salts in comparison with those for **4**. Replacement of the two tetrazole ring protons in **4** with two silver cations in **10** results in a very insoluble compound (in many ways similar to silver azide), which has a similar impact sensitivity to the proton analogue, which is more sensitive to friction (regardless of being a powder) and explodes at the minimum setting in the friction test (<5 N). The nitrate salts with ring protons are all insensitive towards shock and friction (>30 J and >360 N), however, the disilver salt (**11**) shows a much higher sensitivity to impact (15 J) that is similar to secondary explosives, such as TNT (15 J), and to friction (18 N).[52] As for the monosilver 1-MAT and 2-MAT nitrate and perchlorate salts,

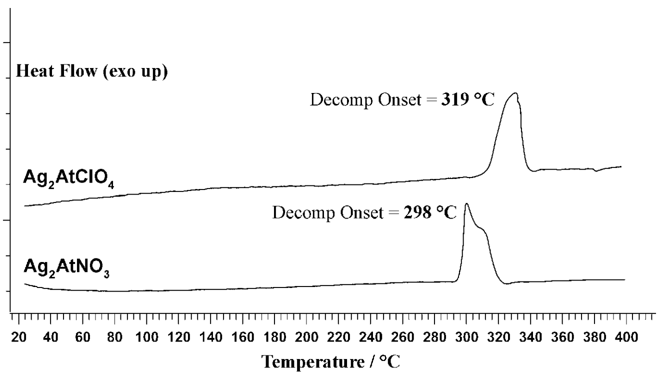


Figure 10. DSC thermograms for disilver derivatives **10** and **11**.

the nitrate salts are impact-sensitive, with values of 10 J (**13**) and 20 J (**15**), and decompose nonexplosively above 100 N in the friction test. On the other hand, the perchlorate salts are either sensitive to impact (**12**, <5 J) or very sensitive (**14**, 2 J). This is keeping in with the logic that hydrated compounds, in this case **12**, tend to be less sensitive to stimuli than anhydrous materials; however, it is surprising that although both **12** and **14** were tested as crystalline materials and both have relatively high impact sensitivity values, in the friction test **12** decomposes nonexplosively in the range 120 to 360 N, whereas **14** explodes at the lowest setting ($<$ 5 N), similarly to powdery **10**. Furthermore, the friction sensitivity values correlate well with the values for sensitivity towards electrostatic discharge; the very sensitive perchlorate salts **4**, **14**, and **10** and nitrate salt **11** explode after initiation by the spark of a Tesla coil. Lastly, all results presented in this section are in agreement with previous studies in our group dealing with perchlorate and nitrate salts of tetrazoles.[2a,11c,44]

Conclusion

A new family of silver-substituted tetrazoles with nitrate or perchlorate anions have been prepared in good yields and purities and characterized by analytical and spectroscopic methods. In addition, the crystal structures of some of the compounds were studied. They show common hydrogen-bonding networks (graph sets) and interesting coordination patterns around the metal center, and represent some of the first examples of silver salts with an azole ligand to have been structurally characterized. The thermal and energetic properties of the new materials are presented herein and compared with those of the parent proton-substituted salts. Replacement of protons by silver cations results in an increase in the sensitivity (some of the compounds show typical primary-explosive behavior) and the decomposition points are markedly increased (>225 °C). The trend in the thermal stability seems to correlate well with the type of ligand (1-MAT < 2-MAT < 5-AT), the anion ($NO_3^- < ClO_4^-$), and the number of silver cations (monosilver < disilver salts). Lastly, the compounds described here have excellent thermal stabilities and some of them can be initiated easily. Regardless of the toxicity associated with the perchlorate anion and to a lesser extend with silver (note that silver is used for cutlery), they provide a more environmentally friendly alternative to commonly used primary explosives based on either mercury (e.g., mercury fulminate) or lead (e.g., lead diazide or styphnate). This is the case for nitrate-anion-based salt **11** in particular.

Experimental Section

Caution! Although we experienced no difficulties with the compounds described here, some of them have sensitivity values that classify them as primary explosives. Appropriate safety precautions should be taken and larger scale syntheses are not recommended. Laboratories and personnel should be properly grounded and safety equipment, such as Kevlar gloves, leather coats, face shields, and ear plugs, is highly recommended.

General: All chemical reagents and solvents were obtained from Sigma–Aldrich Fine Chemicals Inc. or from the chemical store at the LMU, Munich, and were used as supplied. 1-Methyl- and 2-methyl-5-amino-1*H*-tetrazole[9c] and 1,4-dimethyl-5-amino-1*H*-tetrazolium iodide[2a] were synthesized according to previously reported procedures. ^1H, ^{13}C, ^{14}N, and ^{35}Cl NMR spectra were recorded in [D$_6$]DMSO at or near 25 °C by using a JEOL Eclipse 400 instrument operating at 400.18 (^1H), 100.63 (^{13}C), 40.55 (^{14}N), and 39.21 MHz (^{35}Cl). The chemical shifts are given relative to tetramethylsilane (^1H, ^{13}C), nitromethane (^{14}N), and 1.0 M aqueous NaCl (^{35}Cl) as external standards. Infrared (IR) spectra were recorded as KBr pellets at 20 °C by using a Perkin–Elmer Spectrum One FT-IR instrument[53]. Transmittance values are qualitatively described as very strong (vs), strong (s), medium (m), and weak (w). Raman spectra were recorded by using 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 by using a Netsch Simultaneous Thermal Analyzer STA 429. ICP analyses to determine the silver content were performed by using an ICP-AES instrument ($\lambda = 328.068$). Melting points were determined by using DSC (Linseis DSC PT-10 instrument[54] calibrated with standard pure indium and zinc). Measurements were performed in closed aluminum sample pans with a 1 μm hole in the top for gas release under a nitrogen flow of 20 mL min^{-1} and with an identical empty aluminum sample pan as a reference. Mass spectra were recorded on a JEOL MStation JMS 700 instrument in an *m*-NBA matrix by using the FAB$^+$ method.

Synthesis of disilver 5-amino-1*H*-tetrazolium perchlorate (10): 5-Amino-1*H*-tetrazolium monohydrate (0.196 g, 1.8 mmol) was dissolved in concd perchloric acid (4 mL) and a solution of silver perchlorate (0.377 g, 1.8 mmol) in water (1.5 mL) was added dropwise (cloudiness in the solution was observed as the addition proceeded). The clear solution was stirred for 30 min before the addition of water (10 mL). Immediate precipitation of a white (**highly sensitive!**) powder was observed and the reaction mixture was stirred for a further 15 min before the solid was filtered under gravity. This solid was washed five times with water, once with iso-propanol, and once with diethyl ether, then left to air-dry overnight to give the title compound which was carefully weighed (0.522 g, 73 %). DSC (5 °C min^{-1}): 319 °C (decomp); IR (KBr): $\tilde{\nu} = 3414$ (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 cm^{-1} (w); Raman (%): $\tilde{\nu} = 3332$ (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 cm^{-1} (28); elemental analysis calcd (%) for $CH_2N_5O_4ClAg_2$ (399.25): C 3.02, H 0.51, N 17.65, Ag 53.89; found: C 2.88, H 0.72, N 17.90, Ag 53.60.

Synthesis of disilver 5-amino-1*H*-tetrazolium nitrate (11): A solution of silver nitrate (0.832 g, 4.9 mmol) in water (3 mL) was added dropwise to a suspension of 5-amino-1*H*-tetrazolium monohydrate (0.503 g, 4.9 mmol) in concd nitric acid (10 mL). The reaction mixture was stirred for 45 min, then water (10 mL) was added. After a few seconds, cloudiness in the solution was observed and after 15 min a white powder precipitated, which was filtered off under gravity (**very sensitive compound!**) and washed thoroughly with isopropanol and diethyl ether. The product was left to air-dry on a filter paper (1.423 g, 80 %). DSC ($5\,^{\circ}\mathrm{C\,min^{-1}}$): 298 °C (decomp); IR (KBr): $\tilde{\nu}=3416$ (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 $\mathrm{cm^{-1}}$ (w); Raman (%): $\tilde{\nu}=1623$ (9), 1543 (8), 1389 (6), 1295 (28), 1164 (13), 1109 (53), 1040 (100), 779 (16), 710 (7), 459 (10), 184 $\mathrm{cm^{-1}}$ (25); elemental analysis calcd (%) for $CH_2N_6O_3Ag_2$ (359.83): C 3.33, H 0.56, N 23.35, Ag 59.42; found: C 3.13, H 0.78, N 23.60, Ag 59.42.

Synthesis of silver 1-methyl-5-amino-1*H*-tetrazolium perchlorate hemihydrate (12): The perchlorate salt was synthesized analogously to the nitrate derivative by treating 1-methyl-5-amino-1*H*-tetrazole (0.179 g, 1.8 mmol) in concd perchloric acid (3 mL) with a solution of silver perchlorate (0.398 g, 1.9 mmol) in water (3 mL) to give the pure material as a white powder, and recrystallization from hot water afforded single crystals of the compound in high yield (0.342 g, 63 %). DSC ($5\,^{\circ}\mathrm{C\,min^{-1}}$): 102 °C ($-H_2O$); m.p. 154 °C, 252 °C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400.18 MHz, 25 °C, TMS): $\delta=7.02$ (s, 2H; NH_2), 3.74 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.63 MHz, 25 °C, TMS): $\delta=30.1$ (CH_3), 155.6 ppm ($C{-}NH_2$); ^{35}Cl NMR ([D$_6$]DMSO, 39.21 MHz, 25 °C, NaCl): $\delta=+1000$ ppm (ClO_4^-); IR (KBr): $\tilde{\nu}=3326$ (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 $\mathrm{cm^{-1}}$ (m); Raman (%): $\tilde{\nu}=3014$ (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 $\mathrm{cm^{-1}}$ (13); FAB$^+$ (xenon, 6 keV, *m*-NBA matrix): *m*/*z* (%): 206.0 (8) [$C_2H_4N_5Ag$], 208.0 (7) [$C_2H_6N_5Ag$]$^{2+}$, 305.0 (10) [$Ag(C_2H_5N_5)_2$]$^+$; elemental analysis calcd (%) for $C_2H_6N_5O_{4.5}ClAg$ (315.42): C 7.62, H 1.92, N 22.20, Ag 34.20; found: C 7.89, H 1.69, N 22.09, Ag 34.58.

Synthesis of silver 1-methyl-5-amino-1*H*-tetrazolium nitrate (13): A solution of silver nitrate (0.368 g, 2 mmol) in water (4 mL) was added to a solution of 1-methyl-5-amino-1*H*-tetrazole (0.198 g, 0 mmol) in concd nitric acid (3 mL), which resulted in some cloudiness. The mixture was stirred for 20 min and the precipitate formed was filtered off under vacuum, washed with methanol and then with diethyl ether, and dried under high vacuum to give the pure title compound as an insoluble white powder, as confirmed by elemental analysis (0.262 g, 48 %). Recrystallization from hot water gave X-ray-quality crystals of **17** and silver nitrate. DSC ($5\,^{\circ}\mathrm{C\,min^{-1}}$): m.p. 182 °C, 226 °C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400.18 MHz, 25 °C, TMS): $\delta=7.01$ (s, 2H; NH_2), 3.74 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.63 MHz, 25 °C, TMS): $\delta=31.9$ (CH_3), 155.7 ppm ($C{-}NH_2$); ^{14}N NMR ([D$_6$]DMSO, 40.51 MHz, 25 °C, CH_3NO_2): $\delta=-4.3$ ppm (1N; NO_3^-); IR (KBr): $\tilde{\nu}=3402$ (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 $\mathrm{cm^{-1}}$ (w); Raman (%): $\tilde{\nu}=2986$ (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 $\mathrm{cm^{-1}}$ (30); FAB$^+$ (xenon, 6 keV, *m*-NBA matrix): *m*/*z* (%): 206.0 (3) [$C_2H_4N_5Ag$], 208.0 (3) [$C_2H_6N_5Ag$]$^{2+}$, 305.0 (5) [$Ag(C_2H_5N_5)_2$]$^+$; elemental analysis calcd (%) for $C_2H_5N_6O_3Ag$ (268.97): C 8.96, H 1.88, N 31.36, Ag 39.90; found: C 8.90, H 2.09, N 31.19, Ag 39.68.

Silver 2-methyl-5-amino-1*H*-tetrazolium perchlorate (14): Anhydrous silver perchlorate (0.400 g, 1.9 mmol; weighed in a glovebox) was dissolved in water (3 mL) and added to a solution of 2-methyl-5-amino-1*H*-tetrazole (0.179 g, 1.8 mmol) in perchloric acid (70 %, 2 mL). After 15 min, a white powder precipitated and the reaction mixture was quickly heated to reflux for 5 min (not all solid dissolved). Single crystals of the title compound formed upon cooling overnight, and were filtered off, washed thoroughly with acetone and diethyl ether, and left to air-dry (0.357 g, 65 %). DSC ($5\,^{\circ}\mathrm{C\,min^{-1}}$): m.p. 286 °C, 289 °C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400.18 MHz, 25 °C, TMS): $\delta=6.1$ (s, 2H; NH_2), 4.1 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.63 MHz, 25 °C, TMS): $\delta=39.0$ (CH_3), 166.9 ppm ($C{-}NH_2$); ^{35}Cl NMR ([D$_6$]DMSO, 39.21 MHz, 25 °C, NaCl): $\delta=+1000$ ppm (ClO_4^-); IR (KBr): $\tilde{\nu}=3386$ (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 $\mathrm{cm^{-1}}$ (w); Raman (%): $\tilde{\nu}=3246$ (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 $\mathrm{cm^{-1}}$ (20); FAB$^+$ (xenon, 6 keV, *m*-NBA matrix): *m*/*z* (%): 206.0 (6) [$C_2H_4N_5Ag$], 208.0 (5) [$C_2H_6N_5Ag$]$^{2+}$, 305.0 (7) [$Ag(C_2H_5N_5)_2$]$^+$; elemental analysis calcd (%) for $C_2H_5N_5O_4ClAg$ (306.41): C 7.87, H 1.65, N 22.96, Cl 11.47, Ag 35.06; found: C 7.79, H 1.91, N 22.75, Cl 11.30, Ag 35.26.

Silver 2-methyl-5-amino-1*H*-tetrazolium nitrate (15): A solution of silver nitrate (0.385 g, 3 mmol) in water (3 mL) was added dropwise to a solution of 2-methyl-5-amino-1*H*-tetrazole (0.198 g, 0 mmol) in nitric acid (65 %, 2 mL), which resulted in a cloudy solution. This cloudy solution was stirred for 15 min at RT, which caused precipitation of a white powder, then the mixture was quickly heated to reflux for 5 min. Lastly, water (3 mL) was added to the reaction mixture at RT and this was left to stand. The powder that precipitated overnight was filtered off, washed thoroughly with acetone and diethyl ether, and left to air-dry (0.333 g, 62 %). DSC ($5\,^{\circ}\mathrm{C\,min^{-1}}$): m.p. 259 °C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400.18 MHz, 25 °C, TMS): $\delta=6.0$ (s, 2H; NH_2), 4.0 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.63 MHz, 25 °C, TMS): $\delta=38.8$ (CH_3), 166.9 ppm ($C{-}NH_2$); ^{14}N NMR ([D$_6$]DMSO, 40.51 MHz, 25 °C, CH_3NO_2): $\delta=-4.1$ ppm (1N; NO_3^-); IR (KBr): $\tilde{\nu}=3395$ (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 $\mathrm{cm^{-1}}$ (w); Raman (%): $\tilde{\nu}=3215$ (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 $\mathrm{cm^{-1}}$ (11); FAB$^+$ (xenon, 6 keV, *m*-NBA matrix): *m*/*z* (%): 206.0 (3) [$C_2H_4N_5Ag$], 208.0 (3) [$C_2H_6N_5Ag$]$^{2+}$, 305.0 (4) [$Ag(C_2H_5N_5)_2$]$^+$; elemental analysis calcd (%) for $C_2H_5N_6O_3Ag$ (268.97): C 8.96, H 1.88, N 31.36, Ag 39.90; found: C 8.97, H 1.89, N 31.09, Ag 39.65 %.

Bis-(1,4-dimethyl-5-iminotetrazole) silver picrate (16): Picric acid (0.229 g, 1.00 mmol) was dissolved in methanol (5 mL) and treated with neat potassium hydroxide (0.056 g, 1.00 mmol), which resulted in the precipitation of a bright orange solid. The reaction mixture was stirred for 30 min at RT and then reacted with a small excess of anhydrous silver perchlorate (0.249 g, 1.20 mmol; weighed in a glovebox). The immediate precipitation of brown silver picrate (**highly sensitive!**) took place and the reaction mixture was stirred for further 1 h in the absence of light. Then the insoluble solid was filtered off carefully and washed with water (to remove excess $AgClO_4$) and methanol. The methanol-wet silver picrate was carefully transferred into a plastic beaker, suspended in methanol (10 mL), and treated with a solution of 1,4-dimethyl-5-aminotetrazolium iodide (0.193 g, 0.80 mmol) in methanol (5 mL) to give the immediate precipitation of yellow silver iodide. The reaction mixture was stirred for 30 min in the absence of light, then the silver iodide was filtered off, washed with methanol, and discarded. The filtrate was left to slowly evaporate to give two types of yellow single crystals, namely, bright yellow prismic single crystals, which were identified as 1,4-dimethyl-5-aminotetrazolium picrate and light yellow needle-like crystals, which were identified as the title compound. The crystals of **16** (formed as a by-product) were mechanically separated and analyzed (0.012 g, 5 %). ^{1}H NMR ([D$_6$]DMSO, 400.18 MHz, 25 °C, TMS): $\delta=8.58$ (s, 2H; aromatic H), 3.74 (s, 12; CH_3), 3.29–3.43 ppm (brs, 2H; NH); ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.63 MHz, 25 °C, TMS): $\delta=160.9$ (1C; C−O), 149.9 (2C;

C–NH$_2$), 141.8 (2C; C–NO$_2$), 125.2 (2C; C–H), 124.4 (1C; C–NO$_2$), 33.0 ppm (CH$_3$); ^{14}N NMR ([D$_6$]DMSO, 40.55 MHz, 25 °C, MeNO$_2$): $\delta = -12$ ppm (3N; NO$_2$); IR (KBr): $\tilde{\nu} = 3320$ (s), 3070 (m), 2922 (m), 1645 (vs), 1630 (s), 1449 (m), 1395 (s), 1364 (m), 1174 (w), 1053 (w), 1061 (m), 1049 (m), 1030 (m), 975 (w), 712 (w), 690 (w), 578 cm^{-1} (w); Raman (%): $\tilde{\nu} = 3312$ (2), 3078 (16), 2999 (3), 2927 (15), 1566 (41), 1515 (17), 1481 (21), 1366 (27), 1343 (100), 1304 (36), 1290 (66), 1161 (18), 1086 (18), 940 (21), 905 (11), 823 (31), 783 (11), 700 (14), 591 (8), 337 (20), 300 (4), 169 cm^{-1} (14); FAB$^+$ (xenon, 6 keV, *m*-NBA matrix): *m*/*z* (%): 334.0 (12) [Ag(C$_3$H$_7$N$_5$)$_2$]$^+$; FAB$^-$ (xenon, 6 keV, *m*-NBA matrix) *m*/*z* (%): 228.0 (51) [C$_6$H$_2$N$_3$O$_7$]$^-$; elemental analysis calcd (%) for C$_{12}$H$_{16}$N$_{13}$O$_7$Ag (562.21): C 25.63, H 2.87, N 32.39; found: C 25.77, H 2.94, N 32.50.

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 with Dr. M. Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. M. Sucesca (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.

---

[1] a) H.-G. Ang, W. Fraenk, K. Karaghiosoff, T. M. Klapötke, H. Nöth, J. Sprott, M. Suter, M. Vogt, M. Warchhold, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2901–2906; b) K. Karaghiosoff, T. M. Klapötke, A. Michailovski, H. Nöth, M. Suter, *Propellants Explos. Pyrotech.* **2003**, *28*, 1–6; c) J. Geith, T. M. Klapötke, J. Weigand, G. Holl, *Propellants Explos. Pyrotech.* **2004**, *29*, 3–8; d) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *Propellants Explos. Pyrotech.* **2004**, *29*, 325–332; e) T. M. Klapötke, P. Mayer, J. J. Weigand, G. Holl, *Propellants Explos. Pyrotech.* **2005**, *30*, 17–26; f) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *J. Am. Chem. Soc.* **2005**, *127*, 2032–2033; g) J. C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Löhnwitz, P. Mayer, H. Nöth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 4237–4253; h) M. Friedrich, J. C. Gálvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 8044–8052; i) T. M. Klapötke, C. Miró Sabaté, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1017–1024; Sabaté, *Chem. Mater.* **2008**, *20*, 3629–3637; Sabaté, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2671–2677; Sabaté, *Chem. Mater.* **2008**, *20*, 3629–3637; Sabaté, *Chem. Mater.* **2008**, *20*, 3629–3637; j) T. M. Klapötke, C. Miró Sabaté, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2671–2677; k) C. Darwich, T. M. Klapötke, C. Miró Sabaté, *Propellants Explos. Pyrotech.* **2008**, *33*, 336–346; Sabaté, *Chem. Eur. J.* **2008**, *14*, 5756–5771; Sabaté, *Chem. Eur. J.* **2008**, *14*, 5756–5771.

[2] a) K. Karaghiosoff, T. M. Klapötke, P. Mayer, C. Miró Sabaté, A. Penger, J. M. Welch, *Inorg. Chem.* **2008**, *47*, 1007–1019; Sabaté, A. Penger, J. M. Welch, *Inorg. Chem.* **2008**, *47*, 1007–1019; b) A. Hammerl, G. Holl, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* **2002**, *2002*, 834–845; c) A. Hammerl, PhD thesis, Ludwig-Maximilans Universität, München (Germany), **2001**; d) J. J. Weigand, PhD thesis, Ludwig-Maximilans Universität, München (Germany), **2005**; e) J. M. Welch, PhD thesis, Ludwig-Maximilans Universität, München (Germany), **2008**.

[3] a) T. M. Klapötke, P. Mayer, C. Miró Sabaté, A. Penger, J. M. Welch, *233rd ACS Nat. Meet.* (Chicago, IL, United States) **2007**; b) T. M. Klapötke, C. Miró Sabaté, *Proceed. 10th Sem. New Trends Res. Energ. Mater.* (Pardubice, Czech Republic) **2007**; c) H. Xue, Y. Gao, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2005**, *44*, 5068–5072; d) T. M. Klapötke, K. Karaghiosoff, P. Mayer, A. Penger, J. M. Welch, *Propellants Explos. Pyrotech.* **2006**, *31*, 188–195; e) H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2007**, *19*, 1731–1739; f) A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* **2002**, *2002*, 834–845; g) A. Hammerl, G. Holl, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. T. Suter, *Z. Naturforsch. B* **2001**, *56*, 857–870; h) A. Hammerl, T. M. Klapötke, H. Nöth, M. Warchhold, G. Holl, M. Kaiser, U. Ticmanis, *Inorg. Chem.* **2001**, *40*, 3570–3575; i) K. A. Clark, T. M. Klapötke, *230th ACS Nat. Meet.* (Washington, DC, United States) **2005**.

[4] V. A. Ostrovskii, M. S. Pevzner, T. P. Kofman, I. V. Tselinskii, *Targets Heterocycl. Syst.* **1999**, *3*, 467.

[5] R. C. West, S. M. Selby, *Handbook of Chemistry and Physics*, 48th ed., The Chemical Rubber Co., Cleveland, OH, **1967–1968**, pp. D22–D51.

[6] a) S. V. Levchik, A. I. Balabanovich, O. A. Ivashkevich, A. I. Lesnikovich, P. N. Gaponik, L. Costa, *Thermochim. Acta* **1992**, *207*, 115; b) S. V. Levchik, A. I. Balabanovich, O. A. Ivashkevich, A. I. Lesnikovich, P. N. Gaponik, L. Costa, *Thermochim. Acta* **1993**, *225*, 53; c) A. I. Lesnikovich, O. A. Ivashkevich, S. V. Levchik, A. I. Balabanovich, P. N. Gaponik, A. A. Kulak, *Thermochim. Acta* **2002**, *388*, 233; d) A. Gao, Y. Oyumi, T. B. Brill, *Combust. Flame* **1991**, *83*, 345; e) S. V. Levchik, A. I. Balabanovich, O. A. Ivashkevich, P. N. Gaponik, L. Costa, *Polym. Degrad. Stab.* **1995**, *47*, 333.

[7] M. von Denffer, T. M. Klapötke, G. Kramer, G. Spieß, J. M. Welch, G. Heeb, *Propellants Explos. Pyrotech.* **2005**, *30*, 191–195.

[8] T. M. Klapötke, C. Miró Sabaté, J. Stierstorfer, *Z. Allg. Anorg. Chem.* **2008**, submitted.

[9] a) R. J. Spear, *Aust. J. Chem.* **1984**, *37*, 2453–2468; b) C. Stadler, J. Daub, J. Köhler, R. W. Saalfrank, V. Coropceanu, V. Schünemann, C. Ober, A. X. Trautwein, S. F. Parker, M. Poyraz, T. Inomata, R. D. Cannon, *J. Chem. Soc. Dalton Trans.* **2001**, *22*, 3373–3383; c) R. A. Henry, W. G. Finnegan, E. Lieber, *J. Am. Chem. Soc.* **1954**, *76*, 2894–2898.

[10] a) A. Hammerl, T. M. Klapötke, P. Mayer, J. J. Weigand, G. Holl, *Propellants Explos. Pyrotech.* **2005**, *30*, 17–26; b) J. Stierstorfer, T. M. Klapötke, A. Hammerl, R. D. Chapman, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1051–1057.

[11] a) A. Hammerl, M. A. Hiskey, G. Holl, T. M. Klapötke, K. Polborn, J. Stierstorfer, J. J. Weigand, *Chem. Mater.* **2005**, *17*, 3784–3793; b) T. M. Klapötke, P. Mayer, K. Polborn, J. M. Welch, *Proceed. 9th Sem. New Trends Res. Energ. Mater.* (Pardubice, Czech Republic) **2006**, pp. 631–640; c) T. M. Klapötke, P. Mayer, C. Miró Sabaté, J. M. Welch, N. Wiegand, *Inorg. Chem.* **2008**, *47*, 6014–6027.

[12] a) G. Holl, J. J. Weigand, Ger. Offen. 20051006, **2005**; b) A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, H. Piotrowski, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2117–2121.

[13] L. Y. Lee, M. M. Stinecipher, U.S. 5256792, **1993**.

[14] a) K. E. Gutowski, R. D. Rogers, D. A. Dixon, *J. Phys. Chem. B* **2007**, *111*, 4788–4800; b) T. Nakamura, M. Shoji, K. Okada, N. Mayama, A. Yoshikawa, Jpn. Kokai Tokkyo Koho, JP 2006073308, (2006); c) R. Wang, C. M. Jin, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2006**, *45*, 6396–6403; d) A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, P. Mayer, H. Piotrowski, M. Vogt, *Z. Naturforsch. B* **2001**, *56*, 847–856.

[15] a) M. Göbel, K. Karaghiosoff, T. M. Klapötke, C. Miró, J. M. Welch, *Proceed. 9th Sem. New Trends Res. Energ. Mater.* (Pardubice, Czech Republic) **2006**, pp. 202–213; b) H. Xue, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2006**, 2959–2965; c) Y. Gao, H. Gao, C. Piekarski, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2007**, 4965–4972.

[16] J. Charalambous, G. C. Georgious, K. Henrick, *Acta Crystallogr. Sect. C* **1987**, *43*, 659–661.

[17] a) C. Ye, J.-C. Xiao, B. Twamley, J. M. Shreeve, *Chem. Commun.* **2005**, *21*, 2750–2752; b) R. Wang, H. Gao, C. Ye, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2007**, *46*, 932–938; c) Z. Zeng, H. Gao, B.

Twamley, J. M. Shreeve, *J. Mater. Chem.* **2007**, *17*, 3819–3826; d) H. Gao, Z. Zeng, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2008**, *14*, 1282–1290; e) Y. Huang, H. Gao, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2007**, *46*, 2025–2030.

[18] a) T. M. Klapötke, C. Miró Sabaté, J. M. Welch, *Dalton Trans.* **2008** 6372–6380; b) R. J. Spear, P. P. Elischer, *Austr. J. Chem.* **1982**, *35*, 1–13; c) X. C. Xhao, X. Heming, Y. Shulin, *Chem. Phys.* **1992**, *250*, 243–248; d) R. Hagel, U. Bley, Ger. Offen. DE 10221044, **2002**; e) L. R. Bates, *13th Proceed. Symp. Explos. Pyrotech.* **1986**.

[19] a) A. V. Sachivko, V. P. Tverdokhlebov, I. V. Tselinskii, *Zh. Org. Khim.* **1986**, *22*, 206–211; b) M. H. V. Huynh, M. D. Coburn, T. J. Meyer, M. Wetzler, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10322–10327.

[20] a) A. Y. Zhilin, M. A. Ilyushin, I. V. Tselinskii, A. S. Brykov, *Russ. J. Appl. Chem.* **2001**, *74*(1), 99–100; b) A. Y. Zhilin, M. A. Ilyushin, I. V. Tselinskii, *Khim. Fiz.* **2002**, *21*(8), 54–57.

[21] a) M. H. V. Huynh, M. A. Hiskey, T. J. Meyer, M. Wetzler, *Proceed. Nat. Acad. Sci. U.S.A.* **2006**, *103*, 5409–5412; b) M. A. Hiskey, M. H. V. Huynh, U.S. Pat. Appl. Publ. 030715, **2006**; c) L. R. Bates, J. M. Jenkins, U.S. 4094879, **1978**.

[22] W. H. Gilligan, M. J. Kamlet, U.S. NTIS, AD Rep. A036086, **1976**.

[23] a) A. V. Smirnov, M. A. Ilyushin, I. V. Tselinskii, *Russ. J. Appl. Chem.* **2004**, *77*, 794–796; b) A. Y. Zhilin, M. A. Ilyushin, I. V. Tselinskii, A. S. Kozlov, I. S. Lisker, *Russ. J. Appl. Chem.* **2003** *76*, 572–576; c) A. Y. Zhilin, M. A. Ilyushin, I. V. Tselinskii, A. S. Kozlov, N. E. Kuzmina, *Russ. J. Appl. Chem.* **2002**, *75*, 1849–1851.

[24] a) L. G. Lavrenova, V. P. Karavai, S. V. Larionov, V. N. Ikorskii, L. A. Sheludyakova, *Zh. Neorg. Khim.* **1988**, *33*, 2583–2586; b) P. N. Gaponik, S. V. Voitekhovich, A. S. Lyakhov, V. E. Matulis, O. A. Ivashkevich, M. Quesada, J. Reedijk, *Inorg. Chim. Acta* **2005**, *358*, 2549–2557.

[25] a) M. Murotani, H. Mura, M. Takeda, H. Shibafuchi, Eur. Pat. Appl. EPO669325, **1995**; b) A. Katzakian, Jr., H. Cheung, C. E. Grix, D. C. McGehee, PCT Int. Appl. WO 9825868, **1998**; c) S. Jin, Q. Song, *Hanneng Cailiao* **2003**, *11*, 55–56; d) A. Y. Zhilin, M. A. Ilyushin, I. V. Tselinskii, A. S. Brykov, *Russ. J. Appl. Chem.* **2001**, *74*, 96–99; e) M. Gabryszewski, *Pol. J. Chem.* **1993**, *67*, 2081–2084; f) J. R. J. Sorenson, *J. Med. Chem.* **1976**, *19*, 135–148; g) C. E. Vaughan, P. H. Wierenga, G. F. Holland, PCT Int. Appl. WO 2006138733 (2006); h) J. G. Zhang, T. L. Zhang, K. B. Yu, *Huaxue Xuebao* **2001**, *59*(1), 84–90; i) X. He, C. Z. Lu, D. Q. Yuan, *Inorg. Chem.* **2006**, *45*, 5760–5766.

[26] a) A. V. Smirnov, M. A. Ilyushin, I. V. Tselinsky, *Proceed. 3rd Autumn Sem. Propell. Explos. Pyrotech.* Chengdu, China, October 5th–8th, **1999**, 5–9; b) T. S. Konkova, Y. N. Matyushin, A. Vorobev, V. P. Sinditskii, M. D. Dutov, A. E. Fogelzang, *36th Int. Ann. Conf. ICT—Energ. Mater.* **2005**, 93/1–93/13; c) T. S. Konkova, Y. N. Matyushin, A. B. Vorobev, V. P. Sinditskii, M. D. Dutov, *35th Int. Ann. Conf. ICT—Energ. Mater.* **2004** 96/1–96/13; d) X. Zhou, Jpn. Kokai Tokkyo Koho JP 2000297078, **2000**.

[27] a) V. N. Kizhnyaev, V. A. Kruglova, *Zh. Prikl. Khim.* **1992**, *65*, 1879–1884; b) J. R. J. Sorenson, *J. Med. Chem.* **1976**, *19*, 135–148.

[28] a) V. Ernst, T. M. Klapötke, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 879–887; b) T. M. Klapötke, H. Radies, J. Stierstorfer, *Z. Naturforsch. B* **2007**, *62*, 1343–1352.

[29] a) T. M. Klapötke, P. Mayer, K. Polborn, J. Stierstorfer, J. J. Weigand, *Proceed. 9th Sem. New Trends Res. Energ. Mater.* (Pardubice, Czech Republic) **2006**, pp. 641–651; b) G. Geisberger, T. M. Klapötke, J. Stierstorfer, *Eur. J. Inorg. Chem.* **2007**, 4743–4750; c) T. M. Klapötke, P. Mayer, K. Polborn, J. Stierstorfer, J. J. Weigand, *Proceed. 9th Sem. New Trends Res. Energ. Mater.* (Pardubice, Czech Republic) **2006**; d) T. M. Klapötke, J. Stierstorfer, A. U. Wallek, *Chem. Mater.* **2008**, *20*, 4519–4530.

[30] C. T. Rittenhause, US 3663553, **1972**.

[31] a) J. N. Maycock, V. R. P. Verneker, C. S. Gorzynski, Jr., *Spectrochim. Acta A* **1967**, *23*, 2849–2853; b) S. Zeman, M. Dimun, S. Truchlik, V. Kabatova, *Thermochim. Acta* **1984**, *80*, 137–141.

[32] a) J. Duguet, US 4566921, **1986**; b) A. Hammerl, G. Holl, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* **2002**, *4*, 834–845; c) T. M. Klapötke, C. Miró Sabaté, *Chem. Mater.* **2008**, *20*(5), 1750–1763.

[33] a) K. Williamson, P. Li, J. P. Devlin, *J. Chem. Phys.* **1968**, *48*, 3891–3896; b) J. R. Fernandes, S. Ganguly, C. N. R. Rao, *Spectrochim. Acta A* **1979**, *35*, 1013–1020.

[34] a) H. Cohn, *J. Chem. Soc.* **1952**, 4282–4284; b) O. Redlich, E. K. Holt, J. Biegeleisen, *J. Am. Chem. Soc.* **1944**, *66*, 13–16.

[35] N. B. Colthup, L. H. Daly, S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, Boston, **1990**.

[36] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford Univ. Press, New York, **1997**.

[37] A. Bigotto, R. Klingendrath, *Spectrochim. Acta A* **1990**, *46*, 1683–1692.

[38] S. V. Levchik, A. I. Balabanovich, O. A. Ivashkevich, A. I. Lesnikovich, P. N. Gaponik, L. Costa, *Thermochim. Acta* **1993**, *225*, 53–65.

[39] G. M. Sheldrick, Programs for Crystal Structure Analysis (Release 97–2), University of Göttingen, Göttingen (Germany), **1998**.

[40] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[41] D. D. Bray, J. G. White, *Acta Crystallogr. Sect. B* **1979**, *35*, 3089–3091.

[42] J. Bernstein, R. E. Davis, L. Shimoni, N. Chang, *Angew. Chem.* **1995**, *107*, 1689–1708; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555–1573.

[43] http://www.ccdc.cam.ac.uk/support/documentation/rpluto/TOC.html.

[44] T. M. Klapötke, C. Miró Sabaté, A. Penger, M. Rusan, J. M. Welch, **2008**, manuscript in preparation.

[45] a) S. L. Zheng, A. Volkov, C. L. Nygren, P. Coppens, *Chem. Eur. J.* **2007**, *13*, 8583–8590; b) A. P. Purdy, R. Gilardi, J. Luther, R. J. Butcher, *Polyhedron* **2007**, *26*, 3930–3938; c) M. L. Simms, J. L. Atwood, D. A. Zatko, *J. Chem. Soc., Chem. Commun.* **1973**, *2*, 46–47.

[46] N. Wiberg, *Holleman-Wiberg, Lehrbuch der Anorganischen Chemie*, Walther de Gruyter, Berlin, **2007**.

[47] a) C. Darwich, T. M. Klapötke, C. Miró Sabaté, *Propellants Explos. Pyrotech.* **2008**, *33*, 336–346; b) T. M. Klapötke, C. Miró Sabaté, *Chem. Mater.* **2008**, *20*, 3629–3637; c) T. M. Klapötke, C. Miró Sabaté, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1017–1024.

[48] 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.

[49] http://www.bam.de.

[50] T. M. Klapötke, C. M. Rienäcker, *Propellants Explos. Pyrotech.* **2001**, *26*, 43–47.

[51] a) H. Xue, Y. Gao, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2005**, *44*, 5068–5072; b) T. M. Klapötke, K. Karaghiosoff, P. Mayer, A. Penger, J. M. Welch, *Propellants Explos. Pyrotech.* **2006**, *31*, 188–195; c) H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2007**, *19*, 1731–1739.

[52] J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, Germany, **1998**.

[53] http://www.perkinelmer.com.

[54] http://www.linseis.net/html_en/thermal/dsc/dsc_pt10.php.

Received: August 12, 2008