Alkali Salts of 1-Methyl-5-nitriminotetrazole – Structures and Properties

Thomas M. Klapötke, Hendrik Radies, and Jörg Stierstorfer

Ludwig-Maximilians Universität München, Department Chemie und Biochemie, Butenandtstraße 5–13, D-81377 München, Germany

Reprint requests to Prof. Dr. Thomas M. Klapötke. E-mail: tmk@cup.uni-muenchen.de

Z. Naturforsch. 2007, 62b, 1343-1352; received July 17, 2007

Alkali salts of 1-methyl-5-nitriminotetrazole (1, 1-MeAtHNO₂) are common intermediates in the synthesis of alkylated nitriminotetrazoles and their derivatives and can be used as brilliant coloring agents in modern pyrotechnics, due to their cations in combination with the high nitrogen contents. The structures of the crystalline state of A^+ 1-MeAtNO₂⁻ · x H₂O (A = Li⁺, x = 1 (2), A = Na⁺ (3), $A = K^+$ (4), $A = Rb^+$ (5) and $A = Cs^+$ (6), all x = 0 were determined using low temperature single crystal X-ray diffraction. In addition, the compounds were characterized using vibrational (IR and Raman) and multinuclear NMR spectroscopy (¹H, ⁷Li, ¹³C, ¹⁴N, ¹⁵N), elemental analysis and differential scanning calorimetry (DSC). Since tetrazoles are known to be promising energetic materials, the heats of formation were calculated using experimentally determined heats of combustion obtained by bomb calorimetry. The sensitivities of all compounds were tested using the BAM drophammer and friction tester showing them to have no sensitivity neither against friction (< 360 N) nor impact (< 50 J). Crystal data: **2**: monoclinic, $P2_1$, a = 3.5152(3), b = 12.3308(9), c = 7.3381(5) Å, $\beta = 92.068(7)^{\circ}, V = 317.86(4) \text{ Å}^3, Z = 2, \delta = 1.756 \text{ g cm}^{-3}; 3: \text{monoclinic}, P2_1/n, a = 3.6071(2), b = 3.607$ 8.3254(5), c = 18.955(1) Å, $\beta = 91.365(6)^{\circ}$, V = 569.07(6) Å³, Z = 4, $\delta = 1.939$ g cm⁻³; 4: monoclinic, $P2_1/c$, a = 3.6310(1), b = 8.6487(2), c = 19.8598(5) Å, $\beta = 94.945(2)^\circ$, V = 621.34(3) Å³, $Z = 4, \delta = 1.948 \text{ g cm}^{-3}$; **5**: monoclinic, $P2_1/n, a = 8.7948(2), b = 10.1640(2), c = 15.0571(3) \text{ Å}, \beta = 92.470(2)^\circ, V = 1344.71(5) \text{ Å}^3, Z = 8, \delta = 2.258 \text{ g cm}^{-3}$; **6**: monoclinic, $P2_1/n, a = 6.3539(1), \beta = 0.258 \text{ g cm}^{-3}$; **6**: monoclinic, $P2_1/n, a = 0.3539(1), \beta = 0.3539$ $b = 13.4762(3), c = 8.2876(2) \text{ Å}, \beta = 99.245(2)^{\circ}, V = 700.42(3) \text{ Å}^3, Z = 4, \delta = 2.618 \text{ g cm}^{-3}.$

Key words: 1-Methyl-5-nitriminotetrazole, Alkali Salts, Crystal Structures, DSC, Pyrotechnics, Calorimetry

Introduction

Metal salts of tetrazoles [1,2] are still an important field of organic and inorganic chemistry due to the theoretical and practical significance of these unique compounds and the diversity of their properties. Derivatives of tetrazoles [3, 4] can be used as energetic materials [5] since most of them are endothermic compounds owing to their high nitrogen content on the one hand and their astonishing thermal stabilities due to the aromaticity on the other [6, 7]. Alkali and alkaline earth metal salts of tetrazoles [8,9] can be used as coloring agents in modern pyrotechnic compositions [10] due to their brilliant flame colors and simple accessibility [11]. One of the most exiting classes of tetrazoles are 5-substituted tetrazoles [12] (Fig. 1) because their properties can be controlled by using different substituents at the carbon atom. While electrondonating groups such as NH₂ [13] or OH [14] yield rather stable compounds, electron-withdrawing groups



Fig. 1. Examples of 5-substituted tetrazoles (A: 5-aminotetrazole (AT), B: 5-hydroxytetrazole, C: 5-Azidotetrazole, D: 5nitriminotetrazole, E: 5-cyanotetrazole, F: 5-nitrotetrazole).

such as NO₂ [15] and CN [16] destabilize the ring system and lead to highly sensitive materials. The extreme

0932-0776 / 07 / 1100-1343 \$ 06.00 © 2007 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

	2	3	4	5	6
Formula	C ₂ H ₅ LiN ₆ O ₃	C ₂ H ₃ N ₆ NaO ₂	C ₂ H ₃ KN ₆ O ₂	C ₄ H ₆ N ₁₂ O ₄ Rb ₂	C ₂ H ₃ CsN ₆ O ₂
M _r	168.06	166.09	182.19	457.15	276.01
Crystal size, mm ³	$0.05 \times 0.12 \times 0.16$	$0.04 \times 0.13 \times 0.15$	$0.08 \times 0.08 \times 0.21$	$0.07 \times 0.08 \times 0.16$	$0.02\times0.05\times0.05$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
<i>a</i> , Å	3.5152(3)	3.6071(2)	3.6310(1)	8.7948(2)	6.3539(1)
<i>b</i> , Å	12.3308(9)	8.3254(5)	8.6487(2)	10.1640(2)	13.4762(3)
<i>c</i> , Å	7.3381(5)	18.9551(11)	19.8598(5)	15.0571(3)	8.2876(2)
β , deg	92.068(7)	91.365(6)	94.945(2)	92.470(2)	99.245(2)
<i>V</i> , Å ³	317.86(4)	569.07(6)	621.34(3)	1344.71(5)	700.42(3)
Ζ	2	4	4	4	4
Т, К	200	200	100	100	100
$\lambda(MoK_{\alpha}), Å$	0.71073	0.71073	0.71073	0.71073	0.71073
$D_{\rm calcd}, {\rm g}{\rm cm}^{-3}$	1.756	1.939	1.948	2.258	2.618
$\mu(MoK_{\alpha}), cm^{-1}$	0.153	0.227	0.810	7.322	5.247
<i>F</i> (000), e	172	336	368	880	512
hkl range	-3:4; -17:17;	-4:2; -10:9;	-4:3; -10:10;	-10:10; -12:12;	-7:7; -16:11;
	-10:6	-23:21	-23:24	-18:18	-10:10
$((\sin\theta)/\lambda)_{\rm max}$, Å ⁻¹	30.0	26.0	26.5	26.0	26.0
Refl. measured	2174	2894	3667	14582	3552
Refl. unique	947	1125	1287	2642	1373
R _{int}	0.041	0.049	0.023	0.042	0.026
Param. refined	114	112	112	201	112
$wR(F^2)/R(F)$ (all reflexions) ^a	0.094/0.040	0.061/0.032	0.057/0.021	0.060/0.024	0.052/0.023
GooF (F^2)	0.89	0.81	1.05	1.01	0.93
$\Delta \rho_{\text{fin}}$ (min/max), e Å ⁻³	-0.27/0.37	-0.31/0.24	-0.32/0.25	-0.50/0.77	-0.75/1.19

Table 1. Crystal structure data for 2-6.

^a $R(F) = \Sigma \left| |F_{o}| - |F_{c}| \right| / \Sigma |F_{o}|, wR(F^{2}) = \left[\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma (w(F_{o})^{2}) \right]^{/2}, \text{ where } w = \left[\sigma^{2}(F_{o}^{2}) + (zP)^{2} + yP \right]^{-1}, P = (F_{o}^{2} - 2F_{c}^{2}) / 3.$

explosive character of 5-azidotetrazole (C) [17] and 5nitriminotetrazole (D) [18, 19] is based more on the energetic azide and nitramine groups than on the electronic influence of these groups on the ring system.

Tetrazoles usually can either be protonated forming tetrazolium salts [20, 21] or deprotonated forming tetrazolates [22]. While deprotonation increases the thermal stability of tetrazoles, a protonation can lower the decomposition temperature. In this work a series of alkali tetrazolates of 1-methyl-5-nitriminotetrazole, a poorly described compound with interesting energetic properties, are presented. Nitriminotetrazoles [23] and nitriminotetrazolates [24–28] are of special interest because they combine both the oxidizer and the energetic nitrogen-rich backbone in one molecule.

Results and Discussion

Synthesis

The synthesis of the alkali 1-methyl-5-nitriminotetrazolates is shown in Scheme 1. All reactions were performed in water, in case of Li^+ and Na^+ the metal hydroxides, in case of K^+ , Rb^+ and Cs^+ the corresponding carbonates were used. Single crystals were ob-



Scheme 1. Synthesis of the compounds 1-6.

tained by recrystallization from water or water-ethanol solutions.

Molecular structures

The molecular structures in the crystalline state were determined using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD detector with an X-ray wavelength of 0.71073 Å. The data collection was performed with the CRYSALIS CCD software [29], the data reduction with the CRYSALIS RED software [30].

	2	3	4	5	6
Distances:					
O1-N6	1.246(4)	1.258(2)	1.267(2)	1.243(3)	1.259(4)
O2-N6	1.253(4)	1.271(2)	1.263(2)	1.256(3)	1.246(4)
N1-N2	1.348(5)	1.347(2)	1.345(2)	1.340(4)	1.351(4)
N2-N3	1.297(5)	1.304(2)	1.298(2)	1.301(4)	1.293(5)
N3-N4	1.361(5)	1.375(2)	1.366(2)	1.367(4)	1.362(5)
N4-C1	1.339(5)	1.331(3)	1.336(2)	1.335(4)	1.320(5)
N1-C1	1.355(5)	1.347(3)	1.352(2)	1.343(4)	1.350(5)
C1-N5	1.374(5)	1.374(3)	1.375(2)	1.381(4)	1.378(5)
N5-N6	1.325(4)	1.311(2)	1.305(2)	1.320(4)	1.328(4)
N1-C2	1.456(5)	1.460(3)	1.463(2)	1.461(4)	1.463(5)
N4–A	2.027(8)			3.027(3)	3.132(3)
01–A	2.087(8)			2.745(2)	3.234(3)
Angles:					
N1-N2-N3	106.9(3)	106.1(2)	106.2(1)	105.9(3)	106.0(3)
N2-N3-N4	111.2(3)	111.2(2)	111.6(1)	111.5(3)	111.8(3)
N3-N4-C1	105.5(3)	105.1(2)	105.2(1)	105.0(3)	105.1(3)
N4-C1-N1	117.2(3)	108.5(2)	108.1(1)	108.1(3)	108.9(3)
N4-C1-N5	134.7(4)	135.0(2)	135.2(1)	134.6(3)	135.9(3)
C1-N5-N6	116.4(3)	116.1(2)	116.7(1)	116.2(3)	117.4(3)
N5-N6-O1	124.2(3)	125.3(2)	124.3(1)	124.2(3)	115.1(3)
O1-N6-O2	119.7(3)	118.7(2)	119.1(1)	120.1(3)	120.8(3)
N4-M-O1	80.0(3)	67.6(1)	56.5(1)	55.6(1)	52.0(1)
Dihedral angles:					
N1-N2-N3-N4	-0.2(4)	-1.1(3)	0.5(2)	-0.3(3)	0.0(4)
C1-N5-N6-O1	-3.7(5)	2.3(4)	-1.5(2)	-0.8(4)	-178.6(3)

Table 2. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for 2-6 with estimated standard deviations in parentheses.



Fig. 2. A view of the formula unit of **2**. (Ellipsoids at the 50 % probability level).

The structures were solved with SIR-92 [31], SIR-97 [32] or SHELXS-97 [33] and refined with SHELXL-97 [34] and finally checked using PLATON [35]. In all structures the hydrogen atoms were located and refined. The absorptions were corrected by a SCALE3 ABSPACK multi-scan method [36]. In the case of the monoclinic space group of **2** the Friedel pairs were merged. All relevant data and parameters of the X-ray measurements and refinements are given in Table 1 [37].

Lithium 1-methyl-5-nitriminotetrazolate (2) crystallizes as the monohydrate in the monoclinic space



Fig. 3. A view of the coordination of the lithium cations in **2** leading to the formation of endless chains.

group $P2_1$ with two molecules in the unit cell. The molecular moiety can be found in Fig. 2. The bond lengths in the planar (torsion angle N1–N2–N3–N4 = $-0.2(4)^\circ$) tetrazolate ring are between 1.297(5) (N2–N3) and 1.361(5) Å (N3–N4). The distance between the atoms C1 and N5 is 1.374(5) Å, which corresponds more to a C=N double bond (1.30 Å) than a C–N single bond (1.48 Å) and is relevant to the nomenclature (nitrimino *vs.* nitraminotetrazole). The nitramine bond length N5–N6 is 1.325(4) Å.

The lithium cations are pentacoordinated by two water molecules at a distance of 2.060(8) Å, by the *N*,*O*-chelating nitriminotetrazolate with d(Li–O1) = 2.092(8) Å, and d(Li–N4) = 2.027(8) Å and the oxy-



Fig. 4. A view of the formula unit of **3**. (Ellipsoids at the 50 % probability level).



Fig. 5. A view of the packing and coordination in **3**. The sodium cations are represented as grey balls.

gen atom O2 of a neighboring tetrazolate $d(\text{Li}-\text{O2}^{i}) = 2.087(8) \text{ Å} [(i) -1 - x, -0.5 + y, -3 - z]$. This coordination results in endless chains with the units bridged by the oxygen atoms of the NO₂ groups as illustrated in Fig. 3.

The sodium salt **3** of 1-methyl-5-nitriminotetrazole crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The bond lengths and angles in the molecular unit (Fig. 4) are similar to those observed in **2** and can be found in Table 2. Again the tetrazolate ring is planar and the nitramine group lies in this plane (torsion angle C1–N5–N6–O1 = $2.3(4)^{\circ}$).

The sodium cations are six-coordinated by the atoms O1 (2.561(2) Å), O2 (2.441(2) Å), N3ⁱ (2.513(3) Å), O2ⁱⁱ (2.430(2) Å), O1ⁱⁱⁱ (2.349(2) Å) and N4ⁱⁱⁱ (2.392(2) Å) building no regular geometry (ⁱx, 1 + y, z; ⁱⁱ-1 + x, y, z; ⁱⁱⁱ2 - x, -0.5 + y, 0.5 - z). The packing (Fig. 5) can be described as a 2-D structure with hooked stacking.

Potassium 1-methyl-nitriminotetrazolate (4) crystallizes analogously to compound 3 in the monoclinic space group $P2_1/c$ with four molecules in the unit cell



Fig. 6. A view of the formula unit of **4**. (Ellipsoids at the 50 % probability level).



Fig. 7. A view of the formula unit of **5**. (Ellipsoids at the 50 % probability level).



Fig. 8. A view of the formula unit of **6**. (Ellipsoids at the 50 % probability level).

and a density of 1.948 g cm^{-3} . There are nearly no differences in the molecular moiety (Fig. 6) as well as in the packing. The relationship to the sodium salt can also be seen in the similar Raman spectra (see below).

The rubidium salt **5** crystallizes in the monoclinic space group $P2_1/n$ with eight molecules in the unit cell and a density of 2.258 g cm⁻³. One molecular unit is illustrated in Fig. 7. The bond lengths and angles are similar to those described above.

Cesium 1-methyl-5-nitriminotetrazolate (6) also crystallizes in the monoclinic crystal system in the space group $P2_1/n$ with four molecules in the unit cell and a density of 2.618 g cm⁻³. The molecular moiety and the nearest coordination distances to the cesium



Fig. 9. A view of the packing of compound **6** including a unit cell. View along the *a* axis; atoms are represented as balls.

cations (d(Cs-O2) = 3.038 Å, d(Cs-N4) = 3.132 Å) can be seen in Fig. 8.

The packing of the structure, in which the cations and anions form 1-D stags along the a axes, is illustrated in Fig. 9.

Vibrational spectroscopy

1 and its salts 2-6 can be easily identified using vibrational spectroscopy (IR and Raman). After deprotonation, the absorption band of the C=N stretching of 1-methyl-5-nitriminotetrazole at 1670-1580 cm^{-1} is found at lower wavenumbers (1500-1550 cm⁻¹). The Raman spectra are shown in Fig. 10. The spectra of the alkali salts contain further characteristic absorption bands, which were assigned by calculating (DFT B3LYP/CC-PVDZ) the vibrational spectra after optimizing the geometry of the anions using the GAUSSIAN 03 software [38]: $3080 - 3000 \text{ cm}^{-1}$ [$v_{\text{sym}}(\text{CH}_3)$], 1480- 1560 cm^{-1} [$v_{asym}(NO_2)$, v(C=N)], $1460-1400 \text{ cm}^{-1}$ $[v_{asym}(CH_3)]$, 1550–1350 cm⁻¹ [v(tetrazolate ring), v (C–N)], 1050–980 cm⁻¹ [v_{sym} (NNO₂)], 1350– 700 cm⁻¹ [v(NCN), v(NN), $\gamma(CN)$, δ (tetrazolate ring)].

NMR spectroscopy

The alkali salts 2-6 were characterized using multinuclear (¹H, ⁷Li, ¹³C, ¹⁴N, ¹⁵N) NMR spectroscopy. All shifts are given with respect to CH₃NO₂ (¹⁴N, ¹⁵N) and TMS (¹H, ¹³C) as external standard. In all cases D₂O was used as solvent. In the ¹H spectra only the methyl protons and in the case of the monohydrate the crystal water can be seen. The ⁷Li spectrum of **2** shows



Fig. 10. Raman spectra of alkali 1-MeAtNO₂ 2-6.



Fig. 11. ¹⁵N NMR spectrum of Na(1-MeAtNO₂).

one signal at -1.00 ppm. The ¹³C NMR spectra show two signals, caused by the methyl groups and the highfield shifted tetrazole carbon atom. For compound **3** the proton-coupled as well as the proton-decoupled NMR spectra (with full NOE) were recorded. The assignments are based on the analysis of the ¹⁵N, ¹H coupling constants and on comparison with literature [23]. The proton-coupled ¹⁵N NMR spectrum of compound **3**, representative for all five alkali salts, is shown in Fig. 11.

Physico-chemical properties

Differential scanning calorimetry

DSC measurements determining the thermal behavior of the alkali 1-methyl-5-nitriminotetrazolate salts were performed in covered Al containers with a nitrogen flow of 20 mL min⁻¹ on a Perkin-Elmer Pyris 6 DSC [39], calibrated by pure indium and zinc standards at a heating rate of 5 °C min⁻¹. The DSC plots in Fig. 12 show the thermal behavior of *ca.* 1.5 mg of 2-6 in the temperature range from 50-400 °C. The salts 2-6 show melting points between 230 and 280 °C followed by decomposition ranges above 300 °C. The lithium salt 2 shows the loss of its crystal water starting at a temperature of 140 °C.

	2	3	4	5	6
Formula	C ₂ H ₅ LiN ₆ O ₃	C2H3N6NaO2	C ₂ H ₃ KN ₆ O ₂	$C_2H_3N_6O_2Rb$	C2H3CsN6O2
Molecular mass, g mol ⁻¹	168.06	166.09	182.19	228.58	276.01
Impact sensitivity, J ^a	> 100 J	> 100 J	> 100 J	> 100 J	> 100 J
Friction sensitivity, N ^b	> 360 N	> 360 N	> 360 N	> 360 N	> 360 N
Flame color	red	yellow	light red	purple	lavender
N, % ^c	50.01	50.60	46.13	37.04	30.75
Ω, % ^d	-37.86	-43.35	-48.30	-38.50	-31.88
Combustion	50.01	50.60	46.13	36.77	30.45
$T_{\text{melt}}, ^{\circ}\text{C}^{\text{e}}$	271	279	239	228	233
Density, g cm ^{-3f}	1.756	1.939	1.948	2.258	2.618
$-\Delta U_{\rm c}$, cal g ^{-1g}	2000	2140	1980	1422	1125
$-\Delta H_{\rm c}^{\circ}$, kJ mol ^{-1h}	1400	1481	1505	1355	1294
$\Delta H_{\rm f}^{\circ}$, kJ mol ⁻¹ⁱ	-401	9	4	-148	-217

Table 3. Physico-chemical properties of alkali salts 2-6.

^{a,b} BAM methods, see refs. [42– 44]; ^c nitrogen content; ^d oxygen balance [45]; ^e temperature of melting by DSC (β = 5 °C); ^f estimated from a structure determination; ^g experimental (constant volume) combustion energy; ^h experimental molar enthalpy of combustion; ⁱ molar enthalpy of formation.



Fig. 12. DSC plots (endo up) of compounds 2-6 (5 °C min⁻¹); melting points, T_{onset} 2: 271 °C, 3: 279 °C, 4: 239 °C, 5: 228 °C, 6: 233 °C.

Bomb calorimetry

For all calorimetric measurements a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb for the combustion of highly energetic materials was used [40]. The samples (ca. 200 mg) were pressed with a well-defined quantity of benzoic acid (ca. 800 mg) to form a tablet, and a Parr 45C10 alloy fuse wire was used for ignition. In all measurements a correction of 2.3 (IT) cal cm⁻¹ for burned wire has been applied, and the bomb was examined for evidence of non-combusted carbon after each run. A Parr 1755 printer was connected to the calorimeter to produce a permanent record of all activities within the apparatus. The reported values are the average of three single measurements. The calorimeter was calibrated by combustion of certified benzoic acid (SRM, 39i, NIST) in an oxygen atmosphere at a pressure of 3.05 MPa. Typical experimental results of the constant volume combustion energy (ΔU_c) of the salts are summarized in Table 3. The standard molar enthalpy of combustion (ΔH_c°) was derived from $\Delta H_c^{\circ} =$

$LiC_2H_3N_6O_2 \cdot H_2O + 2O_2$	\longrightarrow	$1/2 \text{ Li}_2 \text{O} + 2 \text{ CO}_2 (g) + 5/2 \text{ H}_2 \text{O} (I) + 3 \text{ N}_2$
$NaC_2H_3N_6O_2 + 9/4O_2$	>	$1/2 \text{ Na}_2\text{O}_2 + 2 \text{ CO}_2 (g) + 3/2 \text{ H}_2\text{O} (I) + 3 \text{ N}_2$
KC ₂ H ₃ N ₆ O ₂ + 11/4 O ₂		$KO_2 + 2 CO_2 (g) + 3/2 H_2O (I) + 3 N_2$
$RbC_2H_3N_6O_2 + 11/4O_2$	>	$RbO_2 + 2 CO_2 (g) + 3/2 H_2O (I) + 3 N_2$
$CsC_2H_3N_6O_2 + 11/4O_2$	>	$CsO_2 + 2 CO_2 (g) + 3/2 H_2O (I) + 3 N_2$

Scheme 2. Combustion equations of the salts 2-6.

 $\Delta U_{\rm c} + \Delta nRT$ ($\Delta n = \Delta n_i$ (products, g) – Δn_i (reactants, g); Δn_i is the total molar amount of gases in the products or reactants). The enthalpy of formation, $\Delta H_{\rm f}^{\circ}$, for each of the salts was calculated at 298.15 K using the Hess thermochemical cycle and the combustion reactions given in Scheme 2. The heats of formation of the combustion products were obtained from the literature [41].

The results of the determination of the heats of formation show the trend of decreasing in the endothermic character for compounds 2-6. The inclusion of crystal water leads to exothermic heats of formation [9] as it can be seen for compound 2. While the sodium salt is slightly endothermic, the cesium salt is characterized by a strong exothermic character. ΔH_f (kJ mol⁻¹) 2: -401, 3: +9, 4: +4, 5: -148, 6: -217.

Sensitivities and flame colors

The sensitivities of all compounds 1-6 were tested using the BAM drophammer and friction tester [42– 44]. While 1-methyl-5-nitriminotetrazole shows high sensitivity against impact (> 12.5 J) and friction (> 160 N) and should only be handled with appropriate precautions, the alkali salts are sensitive neither towards impact (> 100 J) nor friction (> 360 N). All salts are characterized by a nearly smokeless combustion and the generation of brilliant flame colors, which are based on the alkali cations (Li: red, Na: yellow, K: light red, Rb⁺: purple, Cs⁺: lavender).

Conclusion

From this experimental study the following conclusions can be drawn:

• 1-Methyl-5-nitriminotetrazole can be easily deprotonated using metal hydroxides or carbonates in water forming the corresponding metal salts.

• Single crystals of the products can be obtained by recrystallization from water / ethanol mixtures. The structures in the crystalline state were determined using low temperature X-ray diffraction. Except for the lithium salt which forms a monohydrate, the alkali 1methyl-5-nitriminotetrazolates crystallize without inclusion of crystal water, in the monoclinic system.

• In contrast to the neutral 1-methyl-5-nitriminotetrazole, its salts are sensitive neither towards friction nor impact and show melting points between 230 and 280 °C followed by decomposition ranges above 300 °C. The combustion is nearly smokeless, and brilliant flame colors are produced.

Experimental Section

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics) if not stated otherwise. 5-Aminotetrazole (97%) was purchased from Aldrich. Melting points were measured with a Perkin-Elmer Pyris 6 DSC, using heating rates of 5° min⁻¹. Otherwise melting points were determined with a Büchi Melting Point B-450 apparatus and are not corrected. ¹H and ¹³C spectra were recorded with Jeol Eclipse 270, Jeol EX 400 or Jeol Eclipse 400 instruments. All chemical shifts are quoted in ppm relative to TMS (¹H, ¹³C), CH₃NO₂ (¹⁴N, ¹⁵N) and LiCl (⁷Li). Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument. Raman spectra were measured using a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental analyses were performed with a Netsch STA 429 Simultaneous Thermal Analyzer. Bomb calorimetry was carried out using a Parr 1356 Bomb calorimeter with a Parr 1108CL oxygen bomb. The sensitivity data were obtained using a BAM drophammer and a BAM friction tester.

CAUTION! The prepared 1-methyl-5-nitriminotetrazole is an energetic compound with high sensitivities against heat, impact and friction. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar[®] gloves and ear plugs) should be used during work on **1**. The described alkali 1-methyl-5-nitriminotetrazolates are more temperature-stable compared with compound **1** and show no sensitivities against impact nor friction.

1-Methyl-5-nitriminotetrazole (1)

1-Methyl-5-aminotetrazole (1.98 g, 0.02 mol) was added in small portions to 10 mL of ice-cooled HNO₃ (100 %). After 2 h the ice bath was removed and the solution was stirred for further 20 h. Afterwards the reaction was quenched with 10 mL of cold water and the HNO₃ was removed using high vacuum until the colorless product started to precipitate. The crude product was recrystallized from hot ethanol (2.74 g, 95 % yield) [18].

Lithium 1-methyl-5-nitriminotetrazolate monohydrate (2)

1-Methyl-5-nitriminotetrazole (0.64 g, 4.4 mmol) and lithium hydroxide (0.11 g, 4.4 mmol) were dissolved in 20 mL of warm water. Afterwards the two solutions were combined and the water was evaporated to leave colorless rods (0.41 g, yield 61%). M. p.: 271 °C, 301 °C (dec.). – IR (KBr): v = 3375 (m), 3319 (m), 3041 (w), 2973 (w), 2231 (w), 1668 (w), 1520 (m), 1481 (m), 1422 (m), 1319 (s), 1295 (s), 1242 (m), 1118 (m), 1055 (m), 999 (m), 893 (m), 769 (m), 739 (m), 683 (s), 584 (s) cm⁻¹. - Raman (1064 nm, 200 mW, 25 °C): v = 3314 (2), 3037 (4), 2973 (15), 1522 (100), 1481 (15), 1450 (11), 1427 (21), 1401 (13), 1321 (23), 1297 (20), 1120 (18), 1047 (96), 1000 (5), 896 (12), 777 (13), 689 (22), 498 (15), 362 (8), 298 (28) cm⁻¹. – ¹H NMR (D₂O, 25 °C, ppm): δ = 3.45 (s, crystal water), 3.62 (s, CH₃). - ⁷Li NMR (D₂O, 25 °C, ppm): $\delta = -1.00. - {}^{13}C$ NMR (D₂O, 25 °C, ppm): $\delta = 33.0$ (s, CH₃) 164.4 (s, CN₄). - ¹⁴N NMR (D₂O, 25 °C, ppm): $\delta = -17.8 (NO_2) - C_2 H_5 Li N_6 O_3(168.04)$: calcd. C 14.29, H 3.00, N 50.01; found C 14.27, H 3.10, N 49.95. – ΔU_c = $-2000 \text{ cal g}^{-1} (-1407 \text{ kJ mol}^{-1}).$

Sodium 1-methyl-5-nitriminotetrazolate (3)

1-Methyl-5-nitriminotetrazole (1.44 g, 10 mmol) and sodium hydroxide (0.40 g, 10 mmol) were added to 50 mL of warm water. After stirring at 90 °C for 5 min the water was evaporated. The crude product was recrystallized from a hot ethanol/water mixture (5:1) yielding colorless rods suitable for X-ray diffraction. (1.54 g, yield 93%). M.p.: 278 °C (dec.). – IR (KBr): v = 3049 (w), 2967 (m), 2697 (m), 2378 (w), 1917 (w), 1786 (w), 1513 (s), 1462 (s), 1379 (vs), 1300 (s), 1238 (s), 1113 (m), 1039 (s), 986 (w), 882 (m), 774 (m), 751 (w), 738 (m), 690 (m), 497 (w) cm⁻¹. - Raman (1064 nm, 200 mW, 25 °C): v = 3053 (7), 3025 (9), 2969 (21), 1512 (100), 1468 (50), 1450 (2), 1407 (25), 1375 (36), 1302 (47), 1239 (14), 1116 (24), 1040 (69), 990 (10), 886 (18), 754 (17), 696 (20), 497 (13), 156 (8), 379 (10), 302 (24), 251 (12) cm⁻¹. – ¹H NMR (D₂O, 25 °C, ppm): $\delta = 3.82$ (s, CH₃). – ¹³C NMR (D₂O, 25 °C, ppm): δ = 33.0 (s, CH₃) 157.6 (s, CN₄). – ¹⁴N NMR (D₂O, 25 °C, ppm): $\delta = -17.9$ (NO₂). $-^{15}$ N NMR (D₂O, 25 °C, ppm):

$$\begin{split} \delta &= -7.4 \ (\text{N3}), \ -18.2 \ (\text{NO}_2), \ -23.5 \ (\text{N2}), \ -82.9 \ (\text{N4}), \\ -157.3 \ (\text{N5}), \ -169.7 \ (\text{N1}). \ -C_2\text{H}_3\text{NaN}_6\text{O}_2 \ (166.07): \ \text{calcd.} \\ \text{C} \ 14.46, \ \text{H} \ 1.82, \ \text{N} \ 50.60; \ \text{found} \ \text{C} \ 14.62; \ \text{H} \ 1.73; \ \text{N} \ 50.58. \ - \\ \Delta U_c &= -2140 \ \text{cal} \ \text{g}^{-1}, \ (-1481 \ \text{kJ} \ \text{mol}^{-1}). \end{split}$$

Potassium 1-methyl-5-nitriminotetrazolate (4)

A solution of 1-methyl-5-nitriminotetrazole (1.44 g, 10 mmol) in 30 mL of water was reacted with potassium carbonate (0.69 g, 50 mmol) by heating till the release of CO₂ stopped. After stirring at 90 °C for 5 min the water was evaporated. The crude product was recrystallized from a hot ethanol / water mixture (3:1) yielding colorless crystals suitable for X-ray diffraction (1.71 g, 94 % yield). M. p.: $239 \,^{\circ}C$ (dec.). – IR (KBr): v = 3454 (w), 3046 (w), 2970 (w), 2380 (w), 1508 (s), 1457 (s), 1408 (s), 1382 (s), 1364 (vs), 1355 (vs), 1298 (m), 1229 (m), 1107 (m), 1035 (m), 979 (w), 879 (m), 774 (m), 740 (m), 687 (m), 494 (w) cm⁻¹. – Raman (1064 nm, 200 mW, 25 °C): v = 3033 (4), 3023 (6), 2986 (15), 2968 (26), 1550 (5), 1508 (100), 1462 (58), 1407 (17), 1366 (23), 1353 (21), 1300 (53), 1231 (8), 1109 (22), 1048 (19), 1035 (90), 981 (7), 882 (18), 748 (21), 683 (31), 495 (20), 449 (6), 371 (11), 295 (41), 241 (12), 208 (9), 160 (7) cm⁻¹. – ¹H NMR (D₂O, 25 °C, ppm): δ = 3.87 (s, CH₃). – ¹³C NMR (D₂O, 25 °C, ppm): δ = 32.0 (s, CH₃), 156.2 (s, CN₄). – ¹⁴N NMR (D₂O, 25 °C, ppm): $\delta = -17.9 (NO_2) - C_2 H_3 K N_6 O_2$ (182.19): calcd. C 13.19, H 1.66, N 46.13; found C 13.22, H 1.70, N 46.47. – $\Delta U_{\rm c}$ = $-1980 \text{ cal } \text{g}^{-1}$, (-1505 kJ mol⁻¹).

Rubidium 1-methyl-5-nitriminotetrazolate (5)

To a warm solution of 1-methyl-5-nitriminotetrazole (1.44 g, 10 mmol) in 30 mL of water rubidium carbonate (1.30 g, 5 mmol) was added. The solution was stirred at 90 °C till the release of CO₂ stopped. After evaporation of the solvent, the crude product was recrystallized from a hot ethanol / water (2 : 1) mixture, yielding colorless crystals (2.12 g, 93 % yield). M. p.: 228 °C (dec.). – IR (KBr): v = 3433 (m), 3039 (m), 2968 (w), 2716 (w), 2342 (m), 1509 (s), 1456 (s), 1411 (s), 1380 (s), 1363 (vs), 1349 (vs), 1294 (s), 1230 (s), 1109 (m), 1049 (m), 1033 (m), 982 (m), 881 (m), 774 (m), 754 (m), 739 (w), 728 (m), 700 (m), 687 (s), 494 (w), 460 (w) cm⁻¹. – Raman (1064 nm, 200 mW, 25 °C): v = 3041 (8), 2985 (21), 2970 (26), 1553 (6), 1511 (90),

- P.N. Gaponik, S.V. Voitekhovich, O.A. Ivashkevich, *Russ. Chem. Rev.* 2006, 75, 507-539.
- [2] H. Nöth, W. Beck, K. Burger, Eur. J. Inorg. Chem. 1998, 93–99.
- [3] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. Int. Ed. 2006, 45, 3584–3601.
- [4] T. M. Klapötke, P. Mayer, A. Schulz, J.J. Weigand, Propellants, Explos., Pyrotech. 2004, 29, 325-332.

1462 (46), 1417 (15), 1368 (18), 1348 (29), 1295 (57), 1231 (9), 1112 (26), 1049 (17), 1033 (100), 985 (9), 885 (20), 755 (36), 701 (7), 684 (36), 495 (24), 460 (9), 370 (21), 289 (28), 224 (13), 193 (13), 151 (6) cm⁻¹. – ¹H NMR (D₂O, 25 °C, ppm): δ = 3.87 (s, CH₃). – ¹³C NMR (D₂O, 25 °C, ppm): δ = 33.0 (s, CH₃), 156.2 (s, CN₄). – ¹⁴N NMR (D₂O, 25 °C, ppm): δ = -17.9 (NO₂). – C₂H₃N₆O₂Rb (228.58): calcd. C 10.51, H 1.32, N 36.77; found C 10.52, H 1.32, N 37.04. – ΔU_c : –1422 cal g⁻¹, (–1355 kJ mol⁻¹).

Cesium 1-methyl-5-nitriminotetrazolate (6)

Cesium carbonate (1.63 g, 5 mmol) was added to a solution of 1-methyl-5-nitriminotetrazole (1.44 g, 10 mmol) in 30 mL of water and stirred for 5 min at 90 °C. After the water was evaporated, the crude product was recrystallized from an ethanol / water (1:1) mixture (2.59 g, 94 % yield). M. p.: 233 °C (dec.). – IR (KBr): v = 3446 (m), 3027 (w), 2954 (w), 2342 (w), 1798 (w), 1506 (s), 1458 (s), 1414 (m), 1388 (s), 1336 (vs), 1322 (vs), 1290 (s), 1233 (m), 1102 (m), 1049 (w), 1033 (m), 978 (w), 881 (m), 776 (m), 751 (w), 739 (m), 685 (m), 487 (w) cm⁻¹. – Raman (1064 nm, 200 mW, 25 °C): v = 3028 (6), 2986 (16), 2956 (17), 1559 (5), 1509 (100), 1459 (39), 1415 (11), 1395 (10), 1325 (9), 1294 (50), 1229 (6), 1105 (26), 1049 (17), 1035 (98), 980 (7), 883 (14), 753 (20), 688 (21), 490 (17), 451 (6), 367 (12), 289 (22), 231 (9), 204 (9) cm⁻¹. - ¹H NMR (D₂O, 25 °C, ppm): $\delta = 3.84$ (s, CH₃). – ¹³C NMR (D₂O, 25 °C, ppm): δ = 33.1 (s, CH₃), 156.2 (s, CN₄). – ¹⁴N NMR (D₂O, 25 °C, ppm): $\delta = -17.9$ (NO₂). $- C_2H_3C_5N_6O_2$ (276.01): calcd. C 8.70, H 1.10, N 30.45; found C 8.77, H 1.10, N 30.75. - $\Delta U_{\rm c}$: -1125 cal g⁻¹, (-1294 kJ mol⁻¹).

Acknowledgements

Financial support of this work by the University of Munich (LMU), the Fonds der Chemischen Industrie and the European Research Office (ERO) of the U.S. Army Research Laboratory (ARL) under contract nos. 9939-AN-01 and N 62558-05-C-0027 and the Bundeswehr Research Institute for Materials, Explosives, Fuels, and Lubricants (WIWEB) under contract nos. E/E210/7D002/4F088 and E/E210/4D004/ X5143 is gratefully acknowledged. The authors are indepted to and thank Dr. habil. M.-J. Crawford as well as Mr. Stefan Sproll (M. Sc.) for many helpful discussions.

- [5] T. M. Klapötke in *Moderne Anorganische Chemie*, 3rd ed., (Ed.: E. Riedel), Walter de Gruyter, Berlin, 2007, pp. 99–104.
- [6] a) A. Hammerl, M. A. Hiskey, G. Holl, T. M. Klapötke, K. Polborn, J. Stierstorfer, J. J. Weigand, *Chem. Mat.* 2005, 17, 3784–3793. b) A. Hammerl, G. Holl, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* 2002, 4, 834–845.

- [7] a) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, J. Am. Chem. Soc. 2005, 127, 2032 – 2033.
- [8] V. Ernst, T. M. Klapötke, J. Stierstorfer, New Trends in Research of Energetic Materials, Proceedings of the 10th Seminar, Vol. 2, Pardubice (Czech Republic) 2007, pp. 575–593.
- [9] V. Ernst, T. M. Klapötke, J. Stierstorfer, Z. Anorg. Allg. Chem. 2007, 633, 879–887.
- [10] J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, **1998**, p. 138.
- [11] a) D. E. Chavez, M. A. Hiskey, M. H. Huynh, D. L. Naud, S. F. Son, B. C. Tappan, *J. Pyrotech.* 2006, 23, 70-80; b) D. E. Chavez, M. A. Hiskey, D. L. Naud, *J. Pyrotech.* 1999, 10, 17-36; c) M. A. Hiskey, D. E. Chavez, D. L. Naud, U.S. patent, 2001, US 6214139.
- [12] Z. P. Demko, K. B. Sharpless, J. Org. Chem. 2001, 66, 7945 – 7950.
- [13] J. Thiele, *Liebigs Ann.* **1892**, 270, 1–2.
- [14] K. Hattori, E. Lieber, J. P. Horwitz, J. Am. Chem. Soc. 1956, 78, 411–15.
- [15] G. I. Koldobskii, D. S. Soldatenko, E. S. Gerasimova, N. R. Khokhryakova, M. B. Shcherbinin, V. P. Lebedev, V. A. Ostrovskii, *Russ. J. Org. Chem.* **1997**, *33*, 1771– 1783
- [16] E. Oliveri-Mandala, T. Passalaqua, *Gazzetta Chim. Ital.* 1912, 41, 430–435.
- [17] a) A. Hammerl, T. M. Klapötke, *Inorg. Chem.* 2002, *41*, 906–912; b) A. Hammerl, T. M. Klapötke, P. Mayer, J. J. Weigand, *Propellants, Explos., Pyrotechn.* 2005, *30*, 17–26.
- [18] T. M. Klapötke, J. Stierstorfer, New Trends in Research of Energetic Materials, Proceedings of the 10th Seminar, Vol. 2, Pardubice (Czech Republic) 2007, pp. 674–690.
- [19] A. M. Astakhov, R. S. Stepanov, L. A. Kruglyakova, A. A. Nefedov, *Russ. J. Org. Chem.* 2001, 37, 577– 582.
- [20] J.C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T.M. Klapötke, K. Loehnwitz, P. Mayer, H. Noeth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* 2005, 44, 4237–4253.
- [21] H. Xue, B. Twamley, J. M. Shreeve, *Inorg. Chem.* 2004, 43, 7972 – 7977.
- [22] C. Ye, J.-C. Xiao, B. Twamley, J. M. Shreeve, *Chem. Commun.* 2005, 21, 2750–2752.
- [23] K. Karahiosoff, T. M. Klapötke, P. Mayer, H. Piotrowski, K. Polborn, R. L. Willer, J. J. Weigand, *J. Org. Chem.* **2006**, *71*, 1295–1305.
- [24] B. C. Tappan, R. W. Beal, T. B. Brill, *Thermochimica Acta* **2002**, 288, 227–232.
- [25] B. C. Tappan, C. D. Incarnito, A. L. Rheingold, T. B. Brill, *Thermochimica Acta* 2002, 384, 113–120.
- [26] T. B. Brill, B. C. Tappan, R. W. Beal, New Trends in Research of Energetic Materials, Proceedings of the 4th

Seminar, Pardubice (Czech Republic), 2001, pp. 17–21.

- [27] A. M. Astakhov, A. D. Vasilev, M. S. Molokeev, A. M. Sirotinin, L. A. Kruglyakova, R. S. Stepanov, *Zh. Strukt. Khim. (Russ.)* 2004, 45, 175–180.
- [28] A. D. Vasilev, A. M. Astakhov, A. A. Nefedov, R. S. Stepanov, Zh. Strukt. Khim. (Russ.) 2003, 44, 359– 361.
- [29] CRYSALIS CCD, Oxford Diffraction Ltd., version 1.171.27p5 beta (release 01-04-2005 CrysAlis171 .NET).
- [30] CRYSALIS RED, Oxford Diffraction Ltd., version 1.171.27p5 beta (release 01-04-2005 CrysAlis171 .NET).
- [31] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, SIR-92, J. Appl. Cryst. 1993, 26, 343.
- [32] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR-97, J. Appl. Crystallogr. 1999, 32, 115.
- [33] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) 1997.
- [34] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) 1997.
- [35] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) 1999.
- [36] SCALE3 ABSPACK, An Oxford Diffraction program (version 1.0.4, gui:1.0.3), Oxford Diffraction Ltd., Oxford (U.K.) 2005.
- [37] CCDC 643232 (2), 643231 (3), 643233 (4), 643234 (5) and 643235 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.
- [38] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Or-

tiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03 (revision A.1), Gaussian Inc., Pittsburgh, PA (USA) **2003**.

- [39] Perkin Elmer Pyris6 DSC, (version 6.0), Perkin Elmer Inc., Waltham, Massachusetts (USA) 2003: http://www.perkinelmer.com/.
- [40] Parr 1356 Isoperibol Bomb Calorimeter, Operating Instruction Manual No. 369M, Parr Instrument Company, Moline, Illinois (USA): http://www.parrinst.de/.
- [41] a) A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101st ed., Walter de Gruyter,

Berlin, **1995**, pp. 250, 859 and 1176; b) http://webbook.nist.gov/chemistry/.

- [42] Impact: Insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 , 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.
- [43] a) M. Sućeska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/.
- [44] T. M. Klapötke, C. M. Rienäcker, Propellants, Explos., Pyrotech. 2001, 26, 43.
- [45] Oxygen balance: Ω (%) = (O 2C H/2 xAO) 1600 M⁻¹; M = molecular mass.