

Alkali metal 5-nitrotetrazolate salts: prospective replacements for service lead(II) azide in explosive initiators†‡

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A family of sensitive energetic salts of the 5-nitrotetrazolate anion with alkali metal cations (Li^+ **1**, Na^+ **2**, K^+ **3**, Rb^+ **4** and Cs^+ **5**) were synthesized either by the digestion of an acid copper salt of 5-nitrotetrazole with a suitable metal hydroxide, or alternatively by reaction of ammonium 5-nitrotetrazolate with a suitable metal base (MOH , MHCO_3 or M_2CO_3) in aqueous or alcoholic solution. All the compounds were characterized by analytical methods (elemental analysis and mass spectrometry) and spectroscopic methods (NMR and vibrational spectroscopy). The lighter metal salts **1** and **2**, incorporate three and two crystal water molecules in the structure, respectively, whereas the heavier alkali metal derivatives form anhydrous species, and thus showed enhanced sensitivity to friction and shock. In addition, the crystal structure of each of the new materials was determined by X-ray diffraction techniques (**1** and **3**: monoclinic, $P2_1/c$; **2**: triclinic, $P\bar{1}$; **4**: monoclinic, Cc and **5**: monoclinic, $C2/c$). The thermal stability of compounds **1**–**5** was assessed by differential scanning calorimetry (DSC) measurements showing significant thermal stability. Lastly, the energies of combustion of **1** and **2** were measured experimentally using oxygen bomb calorimetry (**1**, $-1340(15)$ cal g^{-1} and **2**, $-1200(20)$ cal g^{-1}) and was used to calculate their standard molar heats of formation (**1**, $-610(55)$ kJ mol^{-1} and **2**, $-360(65)$ kJ mol^{-1}).

Introduction

Primary explosives are energetic materials, in which detonation is easily initiated by a physical or electrical stimulus. The detonation shockwave generated by a primary explosive is typically used to initiate a larger amount of a less sensitive explosive material (secondary explosive). Therefore, primary explosives are used in small quantities in a wide range of explosive applications. Lead azide and stypnate (often mixed with a variety of other energetic agents) are the most commonly used primary explosives. The harmful effects of lead to human health and the environment are well known and efforts are under way throughout the energetic materials community to develop new primary explosive materials with formulations free of toxic heavy metals and perchlorates. More extensive background information, and details concerning some recent work in this area are presented in the introduction of ref. 1.

Huynh *et al.* investigated several coordination (iron and copper) complexes of the 5-nitrotetrazolate (NT^-) anion as potential replacements for lead-based primaries.¹ We have recently investigated some nitrogen-rich salts of the same anion² and were, in light of the promising properties of the transition metal complexes of

5-nitrotetrazole, interested to see if the simple alkali metal salts of NT^- might also show some desirable properties. In addition, many heterocycle-based salts of NT^- have been investigated recently.^{3–8}

Sodium 5-nitrotetrazolate dihydrate (**2**) was first synthesized by von Herz by treating the insoluble acid copper salt of 5-nitrotetrazole, formed by the diazotation of 5-amino-(1*H*)-tetrazole in the presence of excess nitrite and copper in aqueous solution, with excess sodium hydroxide.⁹ Compound **2** has subsequently served as the source of the 5-nitrotetrazole moiety in a large number of studies,^{9–15} but has never been structurally characterized. In addition, although many heavy metal salts of 5-nitrotetrazole have been thoroughly investigated, none of the other alkali metal salts of 5-nitrotetrazole appear to have been particularly well investigated prior to our work.^{10–12,15–19}

Results and discussion

Synthesis

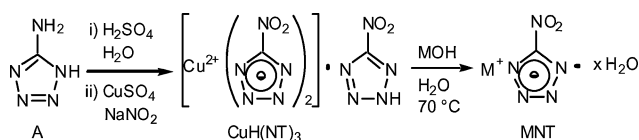
The alkali metal salts **1**–**5** were synthesized by two different methods both starting from 5-amino-1*H*-tetrazole. Initially, the sodium salt **2** was synthesized by the improved von Herz method described by Gilligan *et al.*^{11,12} This method, (method 1) is easily extended to obtain the other alkali metal salts in this study (**1** and **3**–**5**) as shown in Scheme 1. Salts **1** and **2** crystallize as tri- and dihydrated species, respectively, whereas the remaining compounds do not incorporate crystal water and are thus highly sensitive to initiation of detonation by physical stimuli.

In order to enable a practical, larger (~1 g) scale synthesis of the alkali metal salts, an alternative synthesis route, which avoids the direct manipulation of the highly sensitive acid copper salt of 5-nitrotetrazole, was sought. Ammonium 5-nitrotetrazolate (ANT),

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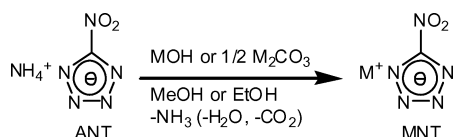
† Electronic supplementary information (ESI) available: Hydrogen bond geometric parameters for **1** and **2** and graph-set matrix for strong hydrogen bonding in **1**. CCDC reference numbers 692851–692855. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811410b

‡ This work has, in part, been presented at the 10th NTREM conference, Pardubice, Czech Republic, April 25–27, 2007, pp. 191–200; 230–239.



Scheme 1 Synthesis of compounds **1–5** by method 1 ($M = \text{Li}$ (**1**, $x = 3$), Na (**2**, $x = 2$), K (**3**, $x = 0$), Rb (**4**, $x = 0$) and Cs (**5**, $x = 0$)).

generated as described in ref. 2 and 20, was treated with a suitable metal hydroxide or carbonate in alcoholic solution, resulting in the formation of gaseous ammonia and/or carbon dioxide and the desired MNT ($M = \text{alkali metal}$) salt as shown in Scheme 2. Lastly, compounds **1–5** are readily soluble in common polar solvents such as water, alcohol, acetone or acetonitrile, are soluble in hot THF and insoluble in non-polar or less polar solvents such as pentane, ether, dichloromethane or chloroform.



Scheme 2 Synthesis of compounds **1–5** by method 2 ($M = \text{Li}$ (**1**), Na (**2**), K (**3**), Rb (**4**) and Cs (**5**)).

NMR and vibrational spectroscopy

Compounds **1–5** were characterized by their NMR (^1H , ^{13}C and ^{14}N) and vibrational (IR and Raman) spectra. In addition, the ^{15}N NMR spectrum of **2** was also measured. The ^1H NMR spectra, in $\text{DMSO}-d_6$, of the hydrated compounds **1** and **2** show a broad signal for the crystal water at $\delta \sim 3.5$ ppm. In the ^{13}C NMR, the resonance for the ring-carbon is observed at $\delta \sim 169$ ppm, which is shifted to lower field when compared to the ring-carbon in the alkali metal salts of 5-amino-1H-tetrazole²¹ and to higher field when compared to the ring-carbon in the metal salts of the 5,5'-azotetrazolate anion.²² The ^{13}C shift of the ring carbon is also identical to that observed in other NT^- containing salts.^{2–8} Due to the high symmetry of the anion, three distinct ^{14}N NMR resonances at $\delta \sim +20$ (N2, N3), -20 (NO_2) and -60 (N1, N4) ppm are observed and are broad ($\nu_{1/2} \sim 420$, 60 and 400 Hz, respectively). As expected, the sharper ^{15}N NMR resonances of **2** ($\delta = +14$, -25 and -66 ppm) are in perfect agreement with those of the ^{14}N NMR (Fig. 1).

The most significant IR and Raman frequencies are tabulated with their corresponding assignments (by comparison to the calculated values²) in Table 1. The Raman spectra of compounds **1–5** are dominated by three strong bands: *ca.* 1420 cm^{-1} , 1060 cm^{-1} and 1030 cm^{-1} and are observed as one strong and two medium bands at *ca.* 1420 , 1050 and 1025 cm^{-1} in the IR spectra. In addition, the IR spectra are dominated by the nitro group asymmetric stretching ($\sim 1540\text{ cm}^{-1}$), the nitro-group and N1–C–N4 (out-of-phase) symmetric stretching ($\sim 1320\text{ cm}^{-1}$) and the nitro-group and N1–C–N4 (in-phase) deformation ($\sim 840\text{ cm}^{-1}$) modes.

X-Ray structures

As shown in Table 5, compound **2** crystallizes with a triclinic unit cell (space group $P\bar{1}$), whereas the remaining salts have monoclinic

Table 1 Calculated (ν_{calcd}) and measured (ν_{measd}) IR and Raman frequencies with assignments

	$\nu_{\text{calcd}}/\text{cm}^{-1a}$	$\nu_{\text{measd}}/\text{cm}^{-1b}$ (IR/Raman)	Mode assignments ^c
1	1538	1540/1540	$\nu_{\text{as}}(\text{NO}_2)$
2	1396	1440/n.o.	$\nu_{\text{as}}(\text{N1–C–N4})$
3	1383	1420/1420	$\nu_{\text{s}}(\text{NO}_2) + \nu_{\text{s}}(\text{N1–C–N4})$, “in-phase”
4	1294	1320/1320	$\nu_{\text{s}}(\text{NO}_2) + \nu_{\text{s}}(\text{N1–C–N4})$, “out-of-phase”
5	1182	1170/1160	$\nu_{\text{as}}(\text{ring})$
6	1163	1160/n.o.	$\nu_{\text{s}}(\text{ring}) + \nu_{\text{s}}(\text{NO}_2)$, “in-phase”
7	1024	1050/1060	$\delta(\text{N1–C–N4}) + \nu_{\text{s}}(\text{NO}_2)$, “in-phase”
8	1018	1025/1030	$\delta_{\text{as}}(\text{ring})$
9	821	840/840	$\delta(\text{NO}_2) + \delta(\text{N1–C–N4})$, “in-phase”
10	763	770/770	$\gamma(\text{NO}_2) + \gamma(\text{N1–C–N4})$, “out-of-phase”
11	718	730/730	$\gamma(\text{ring})$ “in-phase”
12	664	675/n.o.	$\gamma(\text{ring})$ “out-of-phase”
13	522	530/540	$\omega(\text{NO}_2) + \omega(\text{ring})$, “out-of-phase”
14	439	470/n.o.	$\nu(\text{C–N5}) + \delta(\text{NO}_2)$
15	242	n.o./250	$\omega(\text{NO}_2) + \omega(\text{ring})$, “in-phase”
16	218	n.o./230	$\gamma(\text{N1–C–N4})$

^a Calculated frequencies (B3LYP/aug-cc-pvTZ).² ^b Measured frequencies, average values from IR and Raman spectra of compounds **1–5**, n.o. = not observed. ^c Approximate description of vibrational modes: ν = stretching, δ = in-plane bending, γ = out-of-plane bending, ω = in-plane rocking (see X-ray discussion for labelling scheme).

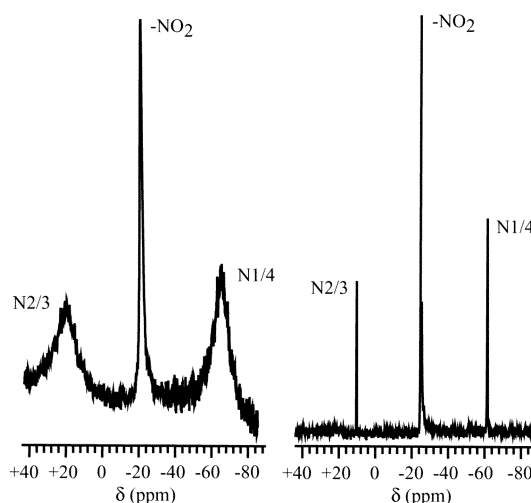


Fig. 1 ^{14}N (left) and ^{15}N NMR (right) spectra of compound **2** in $\text{DMSO}-d_6$.

unit cells in a variety of space groups: $P2_1/c$ (**1** and **3**), Cc (**4**) and $C2/c$ (**5**). A comparison of the lattice parameters and space groups determined seem to indicate no close relationships between the packing of the compounds in this study. However, the lattice parameters determined for **3** show a remarkable (though not wholly unexpected) similarity to those of ammonium 5-nitrotetrazolate, ANT, ($a = 4.8436(2)\text{ \AA}$, $b = 13.7981(6)\text{ \AA}$, $c = 8.0853(4)\text{ \AA}$ and $\beta = 97.256(2)^\circ$, yielding a unit cell volume, V , of $536.03(4)\text{ \AA}^3$ for $Z = 4$).² Further comparison of **3** and ANT follows below.

The 5-nitrotetrazolate anions in **1–5** are, within the limits of structure determination precision, nearly identical (Table 2) as suggested by their vibrational spectra. Furthermore, the anion has the same geometry and has been identified previously.^{2,3,5–8,10,16–19} The tetrazole bond lengths ($\sim 1.33\text{ \AA}$) are all very similar and comparable to other 5-substituted tetrazolate anions with

Table 2 Selected interatomic distances and angles for compounds **1–5**

	1	2	3	4	5
Distances/Å					
C–N4	1.320(1)	1.321(2)	1.320(2)	1.323(9)	1.321(3)
C–N1	1.324(2)	1.322(2)	1.324(2)	1.333(8)	1.319(3)
C–N5	1.444(2)	1.446(2)	1.439(2)	1.453(9)	1.450(3)
N1–N2	1.342(1)	1.338(2)	1.335(2)	1.343(7)	1.345(3)
N2–N3	1.325(1)	1.323(2)	1.328(2)	1.355(9)	1.335(3)
N3–N4	1.345(1)	1.342(2)	1.337(2)	1.331(6)	1.343(3)
N5–O1	1.2289(9)	1.233(2)	1.229(2)	1.223(6)	1.226(3)
N5–O2	1.222(1)	1.214(2)	1.226(2)	1.230(6)	1.230(3)
Angles/°					
N4–C–N1	114.58(7)	115.0(1)	114.9(2)	115.4(6)	116.1(3)
N4–C–N5	122.92(7)	123.2(1)	122.9(2)	123.0(6)	122.2(2)
N1–C–N5	122.50(7)	121.8(1)	122.4(2)	121.6(6)	121.6(2)
C–N1–N2	103.08(7)	102.79(9)	102.6(2)	102.3(5)	102.0(2)
N3–N2–N1	109.69(7)	109.78(9)	110.1(2)	109.6(5)	110.0(2)
N2–N3–N4	109.45(7)	109.75(9)	109.3(2)	109.3(5)	109.3(2)
C–N4–N3	103.20(7)	102.65(9)	103.1(1)	103.4(5)	102.5(2)
O2–N5–O1	125.35(8)	124.8(1)	124.7(2)	124.4(5)	123.9(2)
O2–N5–C	118.20(7)	118.3(2)	117.7(2)	118.8(5)	118.1(2)
O1–N5–C	116.46(7)	116.9(1)	117.6(2)	116.7(5)	117.9(2)

electron-withdrawing substituents^{23,24} and are slightly shorter than found for 5-substituted tetrazolate anions with electron-donating substituents.²¹ In addition, the nitro-group, with the torsion angles N1–C–N5–O2 between 2–5°, is essentially co-planar to the ring in all the structures. Lastly, the coordination geometry²⁵ and contact distances to lithium (**1**), sodium (**2**), potassium (**3**), rubidium (**4**) and cesium (**5**) are in agreement with previously published results.²¹

The packing of compound **1** consists of cation–anion pairs in which the anion chelates a five-coordinate lithium center through O1 and N1 (Fig. 2) and the remaining coordination sites are filled by water molecules (contact distances in Table 3). These cation–anion pairs are joined to one another by a three dimensional network composed of seven strong and medium strength, crystallographically independent O–H...O and O–H...N hydrogen bonds (ESI, Table S1†) as shown in Fig. 2. The shortest contact

Table 3 Metal–ligand contact distances for compounds **1–5**

1		3^b	
Li–N1	2.104(2)	K–N4 ⁱⁱⁱ	2.824(2)
Li–O1	2.735(2)	K–N1 ^{iv}	2.836(2)
Li–O3	1.928(2)	K–N2 ^v	2.847(2)
Li–O4	1.957(2)	K–N3 ^{vi}	2.915(2)
Li–O5	1.999(2)	K–O1	2.950(1)
2^a		K–O2 ^{vii}	2.957(1)
Na–O1 ⁱ	2.466(2)	K–O1 ^{iv}	3.040(2)
Na–O1	2.637(2)	K–O2 ⁱⁱⁱ	3.167(1)
Na–O3	2.371(2)	5^d	
Na–O4	2.387(2)	Cs–N3 ^{xiii}	3.204(2)
Na–N2 ⁱⁱ	2.437(2)	Cs–N2 ^{xiv}	3.210(2)
Na–N1	2.466(2)	Cs–O2 ^{xv}	3.230(2)
4^c		Cs–N4 ^{xiii}	3.303(2)
Rb–O2 ^{viii}	2.925(5)	Cs–O2 ^{vi}	3.333(2)
Rb–O1 ^{ix}	2.939(4)	Cs–N1 ^{xvii}	3.349(2)
Rb–O2 ^x	3.001(5)	Cs–O2 ^{viii}	3.363(2)
Rb–N4 ^{xi}	3.030(4)	Cs–N2 ^{xvii}	3.491(2)
Rb–N1 ^{ix}	3.131(4)	Cs–N3 ^{xiv}	3.608(2)
Rb–N1 ^{xii}	3.136(4)	Cs–N4 ^{xviii}	3.634(2)
Rb–N4 ^x	3.222(4)	Cs–N1	3.325(2)
Rb–N3 ^{xi}	3.479(6)	Cs–O1	3.111(2)
Rb–N2 ^{xiii}	3.519(6)		
Rb–N2	3.028(6)		

^a Symmetry codes for **2**: (i) $-x, -y, 2-z$; (ii) $-x, -y, 1-z$. ^b Symmetry codes for **3**: (iii) $1-x, y-1/2, -z+3/2$; (iv) $x-1, y, z$; (v) $2-x, 1-y, 1-z$; (vi) $2-x, y-1/2, -z+3/2$; (vii) $1-x, 1-y, 2-z$. ^c Symmetry codes for **4**: (viii) $x+1/2, -y+3/2, z+1/2$; (ix) $x, 1-y, z+1/2$; (x) $x+1/2, -y+1/2, z+1/2$; (xi) $x-1/2, y+1/2, z$; (xii) $x, y-1, z$. ^d Symmetry codes for **5**: (xiii) $x, 3-y, z+1/2$; (xiv) $-x, y-1, -z+1/2$; (xv) $-x+1/2, y-1/2, -z+1/2$; (xvi) $-x, y+1/2, y+1/2, -z+1/2$; (xvii) $-x, y, -z+1/2$; (xviii) $x, 2-y, z+1/2$.

distances are, as expected, between lithium and water, followed by the intermediate contact to N1 and the weak contact to O1 of the NT[−] anion. The O2 of the NT[−] anion forms neither strong contacts with the lithium cation, nor strong hydrogen bonds to neighbouring water molecules. The remaining hydrogen bond donors (water molecules) and acceptors (N2, N3, N4 and water molecules) all participate in strong hydrogen bonding, forming a variety of patterns, which are best described using Bernstein's graph-set formalism.^{26,27} The one- and two-bond patterns observed

Table 4 Physical, chemical and energetic properties of compounds **1–5**

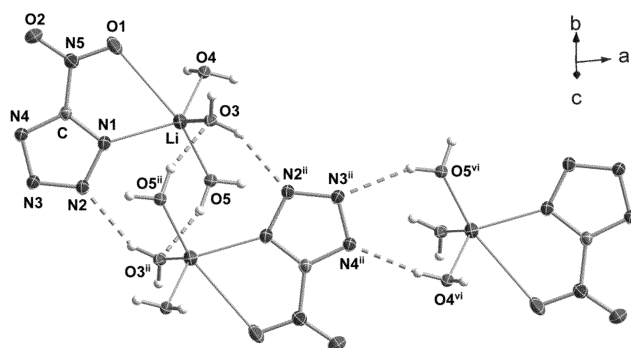
	1	2	3	4	5
Formula	CH ₆ N ₅ O ₅ Li	CH ₄ N ₅ O ₄ Na	CN ₅ O ₂ K	CN ₅ O ₂ Rb	CN ₅ O ₂ Cs
MW/g mol ^{−1}	175.05	173.08	153.16	199.53	246.91
Impact/J ^a	25	>30	10	5	10
Friction/N ^a	324	~360	<5	<5	<5
Flame	Explodes	Explodes	Explodes	Explodes	Explodes
N (%) ^b	40.0	40.5	45.7	35.1	28.4
N + O (%) ^c	85.7	77.5	66.6	51.2	41.3
Ω (%) ^d	−9.1	−9.2	−10.4	−8.0	−6.5
mp/°C ^e	69 (−H ₂ O)	75 (−H ₂ O)	168	146	158
Decomposition/°C ^f	270	200	195	192	194
ρ/g cm ^{−3} ^g	1.609	1.731	2.027	2.489	2.986
−Δ _c U/cal g ^{−1} ^h	1340(15)	1200(20)	n.m.	n.m.	n.m.
−Δ _c H°/kJ mol ^{−1} ⁱ	940(15)	850(20)	n.m.	n.m.	n.m.
−Δ _f H°/kJ mol ^{−1} ^j	610(55)	360(65)	n.m.	n.m.	n.m.

^a Impact and friction sensitivities determined by standard BAM methods²⁸. ^b Nitrogen content. ^c Combined nitrogen and oxygen content. ^d Oxygen balance. ^e DSC onset. ^f Melting and decomposition points (DSC onset) from measurements with β = 2 (**4** and **5**) or 5 (**1–3**) °C min^{−1}. ^g Experimentally determined density (from X-ray). ^h Experimental (constant volume) energy of combustion. ⁱ Experimental molar enthalpy of combustion. ^j Molar enthalpy of formation (n.m. = not measured due to the high sensitivity of the material).

Table 5 Crystallographic data and structure determination details for compounds 1–5

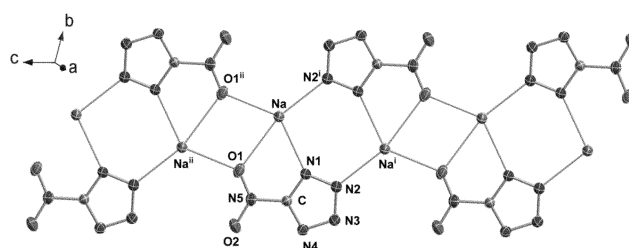
	1	2	3	4	5
Formula	Li[CN ₅ O ₂] \cdot 3H ₂ O	Na[CN ₅ O ₂] \cdot 2H ₂ O	K[CN ₅ O ₂]	Rb[CN ₅ O ₂]	Cs[CN ₅ O ₂]
MW/g mol ⁻¹	175.05	173.08	153.16	199.53	246.91
Crystal System	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	7.6556(1)	6.4266(9)	4.8268(3)	11.9135(5)	15.9926(5)
<i>b</i> /Å	13.0629(2)	7.875(2)	13.1717(8)	5.1626(2)	4.8284(1)
<i>c</i> /Å	7.3543(1)	8.180(3)	7.9423(6)	8.6760(3)	14.7039(4)
α /°	90	104.66(2)	90	90	90
β /°	100.636(2)	109.78(2)	96.363(7)	93.824(4)	104.607(3)
γ /°	90	110.28(2)	90	90	90
<i>V</i> /Å ³	722.83(2)	331.7(2)	501.84(6)	532.43(4)	1098.72(5)
<i>Z</i>	4	2	4	4	8
ρ_{calcd} /g cm ⁻³	1.609	1.731	2.027	2.489	2.986
μ /mm ⁻¹	0.154	0.216	0.976	9.222	6.666
<i>F</i> (000)	360	176	304	376	896
Temperature/K	200(2)	200(2)	200(2)	100(2)	100(2)
Reflections collected	20 900	4683	6536	1591	2974
Unique reflections	2300	1763	1461	875	1191
<i>R</i> _{int}	0.0305	0.0217	0.0273	0.0211	0.0218
Data/restraints/parameters	1750/0/133	1231/0/119	1093/0/82	811/2/83	1058/0/82
GOF	1.093	0.936	0.990	1.031	1.041
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0293, 0.0800	0.0281, 0.0657	0.0241, 0.0553	0.0225, 0.0489	0.0175, 0.0431
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0398, 0.0859	0.0430, 0.0700	0.0407, 0.0601	0.0244, 0.0493	0.0200, 0.0436

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

**Fig. 2** A section of the packing of **1** showing coordination (thin bonds) around the lithium centers, some hydrogen bonding (dashed bonds), atom labels and thermal ellipsoids at 50% probability. Symmetry codes: (ii) 2 - *x*, -*y*, 1 - *z*; (vi) 3 - *x*, -*y*, 1 - *z*.

are exclusively of dimeric nature with only simple D1,1(2) and D2,2(*X*) patterns, where *X* = 2, 4 or 5 found at the primary and secondary levels, respectively. The hydrogen bond geometry as well as a full-graph-set matrix for the strong hydrogen bond patterns are given in the ESI (Table S1 and S3†).

In contrast to compound **1**, the cations (sodium) in compound **2** are eight coordinate with a roughly octahedral structure. Each sodium cation is coordinated by three anions through the equatorial coordination sites (one bidentate and two monodentate) and two water molecules in the axial positions. The equatorial coordination of each sodium cation by three different anions results in the formation of infinite chains of cations and anions (see Fig. 3), which are joined to one another by hydrogen bonding between the axially coordinated water molecules and between the water molecules and N3 and N4 of the NT⁻ anions (Fig. 3). Once again, the water molecules show the strongest coordination to the cation (Table 3) with the anions showing slightly weaker

**Fig. 3** Chain of cations and anions in **2** with atom labels (symmetry codes: (i) -*x*, -*y*, 1 - *z*; (ii) -*x*, -*y*, 2 - *z*) with thermal ellipsoids showing 50% probability.

coordination to the sodium centers. Although the geometric parameters for the hydrogen bonds observed are provided in the ESI (Table S2), due to symmetry ambiguities (for further discussion see X-ray experimental) in the water molecules, the specific hydrogen bond patterns found in the structure of **2** have not been assessed. Compound **3** crystallizes as a water-free solid with a density of 2.033 g cm⁻³, and therefore is a reasonably sensitive energetic material (Table 4). As noted above, the unit cell parameters determined for **3** are very nearly identical to those reported for ammonium 5-nitrotetrazolate (ANT), suggesting strong structural similarities. The packing of **3** is very nearly the same as the packing observed in ANT, as might be expected for cations of similar radii such as ammonium and potassium. Each cation forms contacts (hydrogen bonds in ANT and coordination in **3**) to six anions (Fig. 4) three of which are nearly co-planar with the cation (“co-planar” anions) and three of which form a plane that does not include the cation (“non co-planar” anions). The strongest cation–anion interactions in both structures are observed between the cation and the nitrogen atoms N1, N2 and N4 of the three “co-planar” anions and weaker interactions are observed between the cation and the three “non co-planar” anions

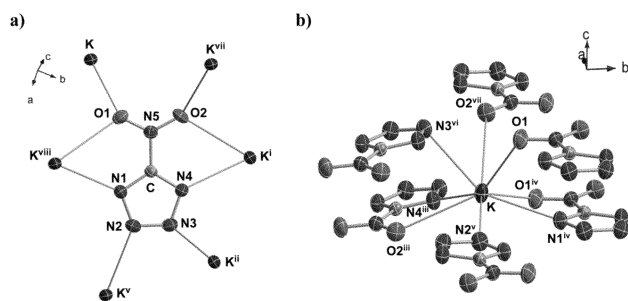


Fig. 4 Packing around the anion (a) and cation (b) in **3** showing cation–anion contacts, atom labels (symmetry codes: (i) $1 - x, 1/2 + y, 3/2 - z$; (ii) $2 - x, 1/2 + y, 3/2 - z$; (iii) $1 - x, y - 1/2, -z + 3/2$; (iv) $x - 1, y, z$; (v) $2 - x, 1 - y, 1 - z$; (vi) $2 - x, y - 1/2, -z + 3/2$; (vii) $1 - x, 1 - y, 2 - z$; (viii) $1 + x, y, z$) and thermal ellipsoids at 50% probability.

(Table 3). In addition, in the structure of **3**, two of the “co-planar” anions also form an additional, weaker contact to the cation by chelation through a nitro-group oxygen atom leading to eight-coordinate potassium centers. The result of these interactions in both **3** and ANT is a structure composed of wave-shaped layers where strong interactions predominate and between them weaker interactions are present. Lastly, all available electron donor atoms in the anion are utilized to form contacts with the cation, indicating a highly efficient packing.

In contrast to compound **3**, the packing of compound **4** appears to be somewhat less efficient. Each anion forms contacts to six different ten-coordinate rubidium centers (Fig. 5). However, in compound **4**, N3 does not interact significantly with the neighbouring cations. Each cation is also surrounded by six anions, two of which chelate the cation through N1 or N4 and O1 and O2, two of which form two contacts to the cation through neighbouring nitrogen atoms and two of which form only a single contact to the cation (Fig. 5). In addition, in contrast to **1–3** the strongest cation–anion interactions in **4** are observed between the nitro-group oxygen atoms and the rubidium center (Table 3). It would seem that the extreme sensitivity of **4** to physical stimuli (Table 4) is potentially explained by the lower packing efficiency, but principally by the weaker cation–anion interactions observed. These weaker interactions might result in higher sensitivity, since

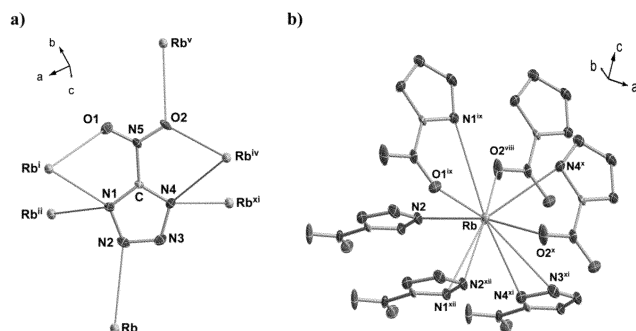


Fig. 5 Packing around the anion (a) and cation (b) in **4** showing cation–anion contacts, atom labels (symmetry codes: (i) $x, 1 - y, -1/2 + z$; (ii) $x, 1 + y, z$; (iv) $-1/2 + x, 1/2 - y, -1/2 + z$; (v) $-1/2 + x, 3/2 - y, -1/2 + z$; (viii) $x + 1/2, -y + 3/2, z + 1/2$; (ix) $x, 1 - y, z + 1/2$; (x) $x + 1/2, -y + 1/2, z + 1/2$; (xi) $x - 1/2, y + 1/2, z$; (xii) $x, y - 1, z$) and thermal ellipsoids at 50% probability.

stimulus energy is less efficiently dissipated in compounds with weaker intermolecular and interionic interactions.

The crystal packing of compound **5** shows a return to a higher efficiency network of cation–anion interactions. Each potential donor atom in the anion forms at least one contact to a caesium center, resulting in each cation being surrounded by seven different anions as shown in Fig. 6. As was the case in the structure of compound **4**, the shortest cation–anion contacts are observed between the nitro-group oxygen atoms of the anions and cations (see Table 3). The somewhat more efficient network of stronger cation–anion contacts seems to explain the lower sensitivity of **5** as discussed above for the increased sensitivity of compound **4**.

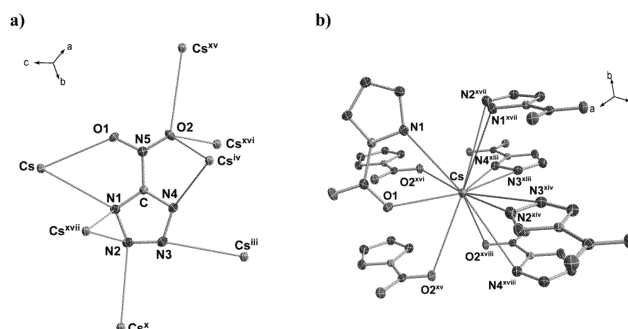


Fig. 6 Packing around the anion (a) and cation (b) in **5** showing cation–anion contacts, atom labels (symmetry codes: (iii) $x, 3 - y, -1/2 + z$; (iv) $x, 2 - y, -1/2 + z$; (x) $-x, 1 + y, 1/2 - z$; (xiii) $x, 3 - y, z + 1/2$; (xiv) $-x, y - 1, -z + 1/2$; (xv) $-x + 1/2, y - 1/2, -z + 1/2$; (xvi) $-x + 1/2, y + 1/2, -z + 1/2$; (xvii) $-x, y, -z + 1/2$; (xviii) $x, 2 - y, z + 1/2$) and thermal ellipsoids at 50% probability.

Energetic properties

In order to assess the energetic properties of compounds **1–5**, the thermal stability (melting and decomposition points from DSC measurements), sensitivity to friction, impact, and thermal shock of each salt was experimentally determined (Table 4). In addition, for the less sensitive salts (**1** and **2**), the (constant volume) energy of combustion was determined experimentally using oxygen bomb calorimetry. Lastly, the heats of combustion and formation were back-calculated from the combustion data.

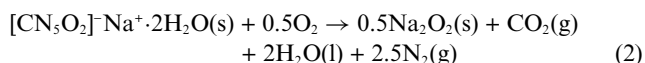
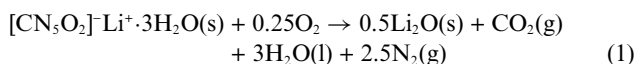
The DSC measurements were made on samples of ~1 mg of each energetic compound in this study (**1–5**) and show a loss of water for the hydrated species **1** and **2** at ~70 °C and melting points, which are generally quite close to the decomposition temperatures. Compounds **1** and **2** show a highly exothermic decomposition without any melting, **3** shows a small melting endotherm prior to the onset of decomposition and **4** and **5** have distinct melting points. Aside from compound **1**, which has a high decomposition temperature of ~270 °C, the remaining materials in this study decompose/explode at ~200 °C (Table 4). The melting and decomposition points of the salts in this study are generally lower than those for the analogous alkali salts of 5-amino-1*H*-tetrazole²¹ or 5,5'-azotetrazolate.²² In comparison to common initiators, such as lead(II) azide ($T_{\text{dec}} = 315$ °C) and lead(II) styphnate ($T_{\text{dec}} = 282$ °C), compounds **1–5** show lower decomposition points.^{1,29} In addition to the DSC analysis, all the compounds were tested by placing a small sample (~0.5–1 mg) of compound in the flame. In all cases this resulted in a loud

explosion (both lead(II) azide and styphnate explode under similar conditions).

The data collected for impact (*i*) and friction (*f*) sensitivity testing are summarized in Table 4. The presence of crystal water in compounds **1** and **2** results in relatively insensitive compounds (*i* > 320 J and *f* > 25 J) whereas the anhydrous species **3–5** are very sensitive to both friction (<5 N = lowest setting) and impact (5–10 J). Dehydration of **1** and **2** under vacuum, at elevated temperature or over P₄O₁₀ under controlled conditions was not successful, however it is apparently possible to dehydrate these species upon removal of solvents (see Experimental, cautionary note).

A comparison of the sensitivity of the materials in this study to those of common explosives is useful in assessing the energetic materials in this study. Compounds **1** and **2** are less sensitive to impact than the secondary explosive TNT (*i* = 15 J) and have similar friction sensitivities to TNT (*f* = 355 N).²⁹ Salts **3–5** show primary explosive properties^{29,30} and have similar sensitivity to both impact and friction as Pb(N₃)₂ (*i* = 3.0–6.5 J, *f* = 0.1–1.0 N for a technical grade material).^{1,29} In addition, the compounds in this study are significantly more sensitive to friction and impact than nitrogen-rich salts containing the NT[–] anion,^{2,4,5} alkali metal salts of 5-amino-1*H*-tetrazole,²¹ and 5-nitroimino-1,4*H*-tetrazole,^{31,32} but are less sensitive than the analogous salts of 5-azido-1*H*-tetrazole.^{33,34} These observations are in keeping with the previously observed sensitivity trends in the salts of 5-substituted tetrazoles (N₃ > NO₂ >> NH–NO₂ > NH₂).³⁵

Due to the sensitive nature of the compounds in this study, the constant volume energies of combustion ($\Delta_c U$) of only the less sensitive lithium and sodium salts were measured using oxygen bomb calorimetry. Measurements for the highly sensitive materials (**3–5**) in this study were not undertaken. The standard molar enthalpy of combustion ($\Delta_c H^\circ$) was calculated from the equation $\Delta_c H^\circ = \Delta_c U + \Delta n RT$ (where Δn is the difference in the number of moles of gases between the products and the reactants). The standard enthalpies of formation of **1** and **2** ($\Delta_f H^\circ$) were back-calculated from the energy of combustion on the basis of the combustion eqn (1) and eqn (2) shown below, Hess' Law and the known standard heats of formation for Li₂O or Na₂O₂, water and carbon dioxide.³⁶ The energies of combustion (**1**: –1340(15), **2**: –1200(20) cal g^{–1}) obtained from sets of four measurements are much more negative than for the analogous salts of 5-amino-1*H*-tetrazole,²¹ whereas the standard heats of formation (**1**: –610(55), **2**: –360(65) kJ mol^{–1}) are comparatively more positive as expected for compounds with more positive oxygen balances.



Experimental

Cautionary note

Several compounds (**3**, **4** and **5**) used in this study are sensitive energetic materials and should only be synthesized and manipulated on a small (<250 mg) scale using proper safety equipment including, but not limited to, thick leather or Kevlar gloves, leather or Kevlar

jackets, face shields and blast screens, ear plugs and plastic or Teflon laboratory equipment. However, the hydrated lithium (**1**), sodium (**2**) and ammonium salts of 5-nitrotetrazole synthesized in this work are generally stable and can be manipulated in larger amounts if proper care is used and the appropriate precautions are taken. Care should be taken not to dehydrate these materials, since the anhydrous materials are dramatically more sensitive and prone to explosion on manipulation. The potassium (**3**), rubidium (**4**) and caesium (**5**) species crystallize without crystal water and are thus extremely sensitive to impact and friction. In addition, although the acid copper salt of 5-nitrotetrazole, which serves as an intermediate in the most currently used processes for the synthesis of 5-nitrotetrazole, could not be initiated by a detonator as a wet solid,^{11,12} has been reported to be extremely sensitive in the dry state, exploding violently when submitted to an electric discharge.^{1,11,12} Therefore, this intermediate should not be isolated and dried in large quantities, but rather always handled when wet.

General

All chemical reagents and solvents were obtained from Sigma Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied. Ammonium 5-nitrotetrazolate was prepared from 5-amino-1*H*-tetrazole according to the literature.^{2,20} ¹H, ¹³C, ¹⁴N and ¹⁵N NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-*d*₆ at or near 25 °C. The chemical shifts are given relative to tetramethylsilane (¹H, ¹³C) or nitromethane (¹⁴N, ¹⁵N) as external standards. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR instrument as KBr pellets at 20 °C. Transmittance values are qualitatively described as 'very strong' (vs), 'strong' (s), 'medium' (m) and 'weak' (w). Raman spectra were recorded on a Perkin-Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported as percentages of the most intense peak and are given in parentheses. CHN elemental analyses of the less sensitive salts **1** and **2** were performed on a Netsch Simultaneous Thermal Analyzer STA 429 and a Varian Vista RL CCD Simultaneous ICP-AES instrument was used to determine the alkali metal content of each compound. Mass spectra were measured on a JEOL MStation JMS 700 instrument. Melting points were determined by differential scanning calorimetry (Perkin-Elmer Pyris 6 DSC instrument, calibrated with a standard of pure indium and zinc). Measurements were performed at a heating rate of 2 or 5 °C min^{–1} 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} with an empty identical aluminum sample pan as a reference.

X-Ray structure determinations

Crystals of compounds **1–5** were obtained as described below. Data sets for **1–5** were collected on an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector. All the data were collected using graphite monochromated MoK α radiation (λ = 0.71073 Å). A multi-scan semi-empirical absorption correction was applied to all data sets collected using the ABSPACK³⁷ software supplied by Oxford Diffraction. All structures were solved by direct methods (SHELXS-97³⁸ and SIR97³⁹) and refined by means of full-matrix least-squares procedures using

SHELXL-97.³⁸ All non-hydrogen atoms were refined anisotropically. For **1**, all hydrogen atoms were located from difference Fourier electron-density maps and refined isotropically. The initial assignment of the space group $P\bar{1}$ for compound **2** seems relatively straight forward, however upon closer inspection, the structure indicates that the assignment of a centrosymmetric ($P\bar{1}$) or non-centrosymmetric ($P1$) space group is ambiguous.^{40–42} The situation observed in the structure of **2** is very nearly identical to that observed in the structure of 1,2-dimethyl-4-nitro-5-morpholinoimidazole monohydrate in that the hydrogen bonded chains of water molecules appear to be “locally non-centrosymmetric homodromic arrays” within a matrix of centrosymmetric cations and anions.⁴³ Therefore, the structure was refined in $P\bar{1}$ and the water molecules were assumed to be disordered.⁴³ Site occupancy factors of H32 and H33 and those of H42 and H43 were fixed at 0.5 and the coordinates were freely refined with fixed isotropic temperature factors set to 0.05 \AA^2 . The resulting structural model yields satisfactory fit statistics (R_1 , wR_2 and GOF), but does accurately describe the homodromic nature of the hydrogen bond network present in the structure. A refinement of **2** in $P1$ was undertaken and this did show an ordered, directional hydrogen bond network. However, due to reasons outlined in Ref. 43, a refinement of the structure of compound **2** in $P1$ was not satisfactory. Compound **4** crystallizes in the non-centrosymmetric space group Cc and was refined as a 60 : 40 racemic twin. The crystallographic data and structure determination details are presented in Table 5. Selected interatomic distances and angles are shown in Table 2. Additionally, hydrogen bond parameters for **1** and **2** are tabulated in the ESI, Table S1 and S2† and the graph-set analysis results for **1** in Table S3†. Lastly, the contact distances between the metal centers and ligands are tabulated in Table 3.

Bomb calorimetry

For the calorimetric measurements, a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 207A oxygen bomb for the combustion of highly energetic materials was used. A Parr 1755 printer, furnished with the Parr 1356 calorimeter, was used to produce a permanent record of all activities within the calorimeter. The samples (~200 mg each) were carefully mixed with ~800 mg analytical grade benzoic acid and pressed into pellets, which were subsequently burned in a 3.05 MPa atmosphere of pure oxygen. The experimentally determined heats of combustion were obtained as the averages of four single measurements with standard deviations calculated as a measure of experimental uncertainty. The calorimeter was calibrated by the combustion of certified benzoic acid in an oxygen atmosphere at a pressure of 3.05 MPa.

Synthesis

Lithium 5-nitrotetrazolate trihydrate (**1**).

Method 1. Compound **1** was synthesized by the modification of method 1 described for compound **2**. 1.40 g (20.29 mmol) sodium nitrite, 0.74 g (2.96 mmol) copper(II) sulfate pentahydrate and 0.57 g (6.71 mmol) 5-amino-1H-tetrazole were used to generate the acid copper salt of 5-nitrotetrazole (as described for compound **2**, method 1) and was subsequently treated with a lithium hydroxide

solution rather than a sodium hydroxide solution resulting in a 42% yield (0.49 g) of compound **1**.

Method 2. Neat lithium hydroxide (0.066 g, 2.76 mmol) was added to a solution of ammonium 5-nitrotetrazolate hemihydrate (0.39 g, 2.76 mmol) in 10 mL (wet) methanol under a stream of nitrogen. The initial suspension turned into a clear solution upon heating, which was stirred over 18 h at reflux (ammonia gas was evolved). At this point, the solution was filtered whilst hot under vacuum and the solvent was removed using a rotatory evaporator, yielding **1** as the trihydrated species. No further purification was necessary (0.45 g, 93%). Crystals of the compound suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate solution of **1**. DSC (5°C min^{-1} , $^\circ\text{C}$) ~ 69 (H_2O loss), ~ 270 (mp + decomposition). Found: C 6.7, H 3.6, N 39.7, Li 4.0. $\text{CH}_6\text{N}_5\text{O}_5\text{Li}$ requires C 6.9, H 3.5, N 40.0, Li 4.0%. Raman $\tilde{\nu}/\text{cm}^{-1}$: 3300–3000(2), 1545(10), 1508(4), 1466(7), 1429(100), 1328(8), 1191(5), 1162(5), 1086(47), 1058(32), 839(6), 776(4), 544(3), 449(3) and 243(3). IR $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 3341 vs, 2867 w, 2752 w, 2484 w, 2087 w, 1666 m, 1559 vs, 1506 m, 1468 s, 1431 s, 1405 m, 1384 m, 1327 s, 1190 m, 1161 m, 1082 w, 1057 w, 1040 m, 841 s, 702 s, 662 s and 519 s. δ_{H} (DMSO- d_6 , 400.18 MHz, TMS) 3.51 (s, H_2O). δ_{C} (DMSO- d_6 , 100.63 MHz, TMS) 169.2 (C– NO_2). $\delta_{14\text{N}}$ (DMSO- d_6 , 28.89 MHz, TMS) +20 (2N, $\nu_{1/2} \sim 430$ Hz, N2/3), –23 (1N, $\nu_{1/2} \sim 60$ Hz, NO_2), –67 (2N, $\nu_{1/2} \sim 400$ Hz, N1/4). MS: m/z (FAB⁺, xenon, 6 keV, m-NBA matrix) 114 ($[\text{NT}]^+$, 100%) and 235 ($[\text{Li}(\text{NT})_2]^+$, 100).

Sodium 5-nitrotetrazolate dihydrate (**2**).

Method 1.^{11,12} 13.70 g (198.6 mmol) of sodium nitrite and 7.24 g (29.0 mmol) copper(II) sulfate pentahydrate were dissolved in 40 mL water in a plastic beaker and cooled in a water–ice bath. A solution of 5.60 g (65.8 mmol) 5-amino-1H-tetrazole, a small amount of copper(II) sulfate pentahydrate and 3.6 mL (68.0 mmol) concentrated sulfuric acid in 80 mL water was added slowly *via* a dropping funnel under vigorous stirring. The dropping funnel was rinsed with a solution of 2.8 mL (53.0 mmol) concentrated sulfuric acid in 10 mL water. After a 30 min reaction time, the precipitated acid copper salt of 5-nitrotetrazole, was carefully vacuum filtered, washed with a solution of 1.6 mL (30.0 mmol) of concentrated sulfuric acid in 32 mL water and thereafter with 32 mL water. The wet cake was carefully transferred to a plastic beaker containing 80 mL water and treated with 20% sodium hydroxide solution until pH > 9, as determined by universal indicator paper. The slurry was heated to 70°C for 1.5 h and the brown/black precipitate (CuO) was filtered whilst hot through wet celite. The pH of the yellow filtrate was adjusted with diluted sulfuric acid to pH 3–4, giving a slightly green solution. The solvent was then carefully removed under vacuum (20 mbar) at 60°C . The yellow solid residue obtained was continuously extracted using a Soxhlet apparatus with 50 mL acetone for 3 h yielding a slightly yellow acetone solution. The solution was cooled to -78°C , resulting in the precipitation of an off-white powder, which was vacuum filtered and washed with diethyl ether yielding 3.51 g of **2**. The remaining acetone solution was transferred to a plastic beaker and left to evaporate, yielding large crystals (suitable for X-ray analysis), which were washed with a little cold acetone and then diethyl ether. 2.70 g of additional pure material was thus obtained. Both crops of material proved to be pure by elemental analysis and confirmed that **2** is isolated as the dihydrated species (total yield: 6.21 g, 55%).

Method 2. Compound **2** was also synthesized as described for compound **1** (method 2) from 0.429 g (3.04 mmol) ammonium 5-nitrotetrazolate hemihydrate and 0.12 g (3.04 mmol) sodium hydroxide in 98% yield (0.52 g). DSC (5 °C min⁻¹, °C) ~75 (H₂O loss), ~200 (decomposition). Found: C 7.1, H 2.3, N 40.4, Na 13.2. CH₄N₅O₄Na requires C 6.9, H 2.3, N 40.5, Na 13.3%. Raman $\tilde{\nu}/\text{cm}^{-1}$: 3300–2900(2), 1555(12), 1452(7), 1419(100), 1321(6), 1173(4), 1068(62), 1053(24), 842(7), 774(5), 543(4), 456(3), 262(3), 150(4). IR $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 3417 s, 2862 w, 2732 w, 2468 w, 2099 w, 1690 m, 1548 vs, 1508 w, 1474 m, 1454 s, 1421 s, 1376 w, 1321 s, 1193 m, 1172 m, 1066 m, 1041 m, 841 s, 665 m, 602 m and 539 m. δ_{H} (DMSO-*d*₆, 400.18 MHz, TMS) 3.50 (s, H₂O). δ_{C} (DMSO-*d*₆, 100.63 MHz, TMS) 169.2 (C–NO₂). $\delta_{14\text{N}}$ (DMSO-*d*₆, 28.89 MHz, TMS) +21 (2N, $\nu_{\frac{1}{2}}$ ~430 Hz, N2/3), –23 (1N, $\nu_{\frac{1}{2}}$ ~60 Hz, NO₂), –60 (2N, $\nu_{\frac{1}{2}}$ ~380 Hz, N1/4). $\delta_{15\text{N}}$ (DMSO-*d*₆, 28.89 MHz, TMS) +14 (2N, s, N2/3), –25 (1N, s, NO₂), –66 (2N, s, N1/4). MS: *m/z* (FAB[–], xenon, 6 keV, m-NBA matrix) 114 ([NT][–], 100%) and 251 ([Na(NT)₂][–], 100).

Potassium 5-nitrotetrazolate (3).

Method 1. Compound **3** was synthesized according to method 1 as described for compound **2** from 1.53 g (22.04 mmol) sodium nitrite, 0.80 g (3.22 mmol) copper(II) sulfate pentahydrate, 0.62 g (7.30 mmol) 5-amino-1*H*-tetrazole and a potassium hydroxide solution. Before rotor evaporating the water solution to dryness, the reaction mixture was divided into two fractions, which were treated separately in order to diminish the hazards involved with the isolation of large amounts of the highly sensitive compound (0.53 g, 48%).

Method 2. Alternatively, **3** was synthesized according to method 2 as described for compound **1** from 0.22 g (1.59 mmol) ammonium 5-nitrotetrazolate hemihydrate and 0.09 g (1.59 mmol) potassium hydroxide. Due to the high sensitivity of the compound, the solvent (methanol) was left to slowly evaporate in a plastic beaker (0.24 g, quantitative yield). Single crystals of the potassium salt were obtained by slow evaporation of a concentrated solution of the compound in acetone. DSC (5 °C min⁻¹, °C) 168 (mp) ~195 (decomposition). Found: K 25.3. CN₅O₂K requires K 25.5%. Raman $\tilde{\nu}/\text{cm}^{-1}$: 1747(1), 1534(9), 1450(2), 1419(100), 1174(3), 1051(20), 1028(52), 843(6), 774(5), 543(2), 260(1), 150(5). IR $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 2691 w, 2411 w, 1991 w, 1833 w, 1586 w, 1527 s, 1483 m, 1441 s, 1435 s, 1429 s, 1404 s, 1340 w, 1307 s, 1163 m, 1152 w, 1108 vs, 1039 w, 1020 w, 997 m, 836 s, 757 m, 723 s, 691 s, 668 m, 524 vs and 457 w. δ_{C} (DMSO-*d*₆, 100.63 MHz, TMS) 169.0 (C–NO₂). $\delta_{14\text{N}}$ (DMSO-*d*₆, 28.89 MHz, TMS) +20 (2N, $\nu_{\frac{1}{2}}$ ~430 Hz, N2/3), –21 (1N, $\nu_{\frac{1}{2}}$ ~60 Hz, NO₂), –66 (2N, $\nu_{\frac{1}{2}}$ ~400 Hz, N1/4). MS: *m/z* (FAB[–], xenon, 6 keV, m-NBA matrix) 114 ([NT][–], 100%) and 267 ([K(NT)₂][–], 100).

Rubidium 5-nitrotetrazolate (4).

Method 1. Compound **4** was synthesized according to method 1 as described for compound **2** from 1.31 g (18.87 mmol) sodium nitrite, 0.69 g (2.76 mmol) copper(II) sulfate pentahydrate, 0.53 g (6.25 mmol) 5-amino-1*H*-tetrazole and a rubidium hydroxide solution. Before rotor evaporating the water solution to dryness, the reaction mixture was divided into two fractions, which were treated separately in order to diminish the hazards involved with the isolation of large amounts of highly sensitive **4** (0.50 g, 41%).

Method 2. Ammonium 5-nitrotetrazolate hemihydrate (0.27 g, 1.94 mmol) was dissolved in 10 mL ethanol and reacted with

rubidium carbonate (0.22 g, 0.97 mmol) and refluxed for 2 d under the exclusion of air. The white insoluble material (rubidium carbonate) was filtered whilst hot and discarded. The product crystallized upon slow cooling to room temperature and the yield could be increased by cooling the mother liquors further. Compound **4** was **carefully** gravity-filtered and washed with cold ethanol and ether (0.23 g, 59%). Suitable crystals for X-ray crystal structure analysis were obtained by cooling the mother liquors in a refrigerator. DSC (2 °C min⁻¹, °C) 146 (mp), ~192 (decomposition). Found: Rb 42.5. CN₅O₂Rb requires Rb 42.8%. Raman $\tilde{\nu}/\text{cm}^{-1}$: 1546(7), 1418(100), 1319(4), 1161(3), 1052(42), 1027(34), 842(6), 773(3), 542(3), 253(4), 156(3). IR $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 2854 w, 2442 w, 2025 w, 1546 s, 1507 w, 1444 s, 1417 s, 1316 s, 1171 m, 1159 m, 1108 w, 1050 m, 1025 m, 838 s, 668 m and 528 w. δ_{C} (DMSO-*d*₆, 100.63 MHz, TMS) 168.9 (C–NO₂). $\delta_{14\text{N}}$ (DMSO-*d*₆, 28.89 MHz, TMS) +20 (2N, $\nu_{\frac{1}{2}}$ ~430 Hz, N2/3), –22 (1N, $\nu_{\frac{1}{2}}$ ~50 Hz, NO₂), –64 (2N, $\nu_{\frac{1}{2}}$ ~400 Hz, N1/4). MS: *m/z* (FAB[–], xenon, 6 keV, m-NBA matrix) 114 ([NT][–], 100%) and 314 ([Rb(NT)₂][–], 100).

Caesium 5-nitrotetrazolate (5).

Method 1. Compound **5** was synthesized according to method 1 as described for compound **2** from 1.15 g (16.68 mmol) sodium nitrite, 0.61 g (2.44 mmol) copper(II) sulfate pentahydrate, 0.47 g (5.53 mmol) 5-amino-1*H*-tetrazole and a caesium hydroxide solution. Before rotor evaporating the water solution to dryness, the reaction mixture was divided into two fractions, which were treated separately in order to diminish the hazards involved with the isolation of large amounts of highly sensitive **5** (0.62 g, 46%).

Method 2. Ammonium 5-nitrotetrazolate hemihydrate (0.25 g, 1.77 mmol) was dissolved in 10 mL ethanol before caesium carbonate (0.29 g, 0.88 mmol) was added to it to form a suspension. After a 24 h reaction time at reflux, the reaction mixture formed a solution and the insoluble powdery material (caesium carbonate) was filtered when the solution was still hot and discarded. Compound **5** precipitates immediately out of the hot reaction mixture when left to cool slowly to room temperature as feathery crystals, which were used to determine the crystal structure. The solvent was left to evaporate slowly at room temperature and the residue was **carefully** recrystallized from the minimum amount of hot ethanol (0.38 g, 87%). DSC (2 °C min⁻¹, °C) 158 (mp), ~194 (decomposition). Found: Cs 53.6. CN₅O₂Cs requires Cs 53.8%. Raman $\tilde{\nu}/\text{cm}^{-1}$: 1530(16), 1419(100), 1316(11), 1056(51), 1031(28), 840(13), 733(10), 535(10), 230(9). IR $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 2723 w, 2444 w, 2055 w, 1847 w, 1633 m, 1528 s, 1505 m, 1420 s, 1384 s, 1314 s, 1170 m, 1151 m, 1105 m, 1054 m, 1030 m, 1022 w, 876 w, 840 s, 774 w, 730 w, 676 m, 615 w, 559 w and 467 w. δ_{C} (DMSO-*d*₆, 100.63 MHz, TMS) 168.7 (C–NO₂). $\delta_{14\text{N}}$ (DMSO-*d*₆, 28.89 MHz, TMS) +21 (2N, $\nu_{\frac{1}{2}}$ = 410 Hz, N2/3), –22 (1N, $\nu_{\frac{1}{2}}$ = 60 Hz, NO₂), –62 (2N, $\nu_{\frac{1}{2}}$ = 380 Hz, N1/4). MS: *m/z* (FAB[–], xenon, 6 keV, m-NBA matrix) 114 ([NT][–], 100%) and 361 ([Cs(NT)₂][–], 100).

Conclusions

Alkali metal salts with the energetic 5-nitrotetrazolate anion were synthesized by two different methods and fully characterized, including X-ray structure analysis. DSC analyses showed good thermal stabilities up to (at least) ~200 °C. Standard tests were used to assess the sensitivity of the materials to classical stimuli. The salts with the harder lithium and sodium cations contain crystal

water, which is reflected in the low sensitivity of the compounds towards shock and friction, whereas the rest of the salts form as the anhydrous species and thus, show increased sensitivities but are devoid of a toxic metal, such as lead, making them of interest as prospective replacements for commonly used primary explosives.

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