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Alkaline Earth Metal Salts of 5-Nitro-2*H*-tetrazole: Prospective Candidates for Environmentally Friendly Energetic Applications

Thomas M. Klapötke,*[a] Carles Miró Sabaté,[a] and Jan M. Welch[a]

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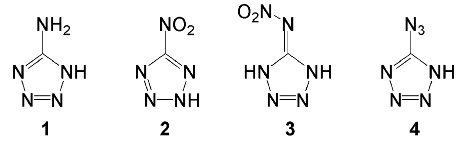
Deprotonation of ammonium 5-nitrotetrazolate in aqueous or alcoholic solution upon reaction with a suitable alkaline earth metal (M^{2+}) hydroxide or carbonate ($M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}$ or Ba^{2+}) leads to the synthesis of a family of sensitive energetic metal salts based on the 5-nitrotetrazolate anion (NT^-). These new compounds were characterized by IR, Raman and NMR (^1H, ^{13}C and ^{14}N) spectroscopy as well as by mass spectrometry and elemental analysis. In addition, the crystal structure of the calcium salt was determined by low-temperature X-ray measurements [orthorombic, space group *Pna*2; $a = 6.8960(2)$, $b = 32.575(1)$, $c = 6.2399(2)$ Å; $V = 1401.73(8)$ Å^3]. All compounds show good thermal stabilities at or above 180 °C, as proved by DSC measurements, and the sensitivity of the salts towards impact and friction increases with the size of the cation (Mg < Ca < Sr < Ba). Lastly, the 5-nitro-2*H*-tetrazole salts presented here show promise for future use as energetic compounds.

Introduction

The interesting energetic properties of tetrazole-based energetic materials have mainly been investigated with a view to using these compounds as propellants and/or secondary explosives,[1,2] and only recently have metal salts with 5-substituted tetrazole ligands been studied as prospective primary explosives.[3] Primary explosives are energetic materials, in which detonation is easily initiated by a physical or electrical stimulus. They have detonation velocities typically in the range of 3500–5500 m s^{-1}, in contrast with secondary explosives, which usually have values between 5500 and 9000 m s^{-1}.[4] The initiation of a primary explosive generates a shock wave, which is transferred and used to detonate a more powerful and less sensitive secondary explosive. Lead-based compounds such as lead azide and styphnate are the most commonly used primary explosives despite the long-term toxicity associated with lead. For this reason, the energetic materials community is trying to develop compounds, which are devoid of toxic metals and/or perchlorates. A more detailed background and some recent work in this area can be found in two key papers.[3]

Hiskey and co-workers[3b] have investigated several iron and copper complexes of 5-nitro-2*H*-tetrazole (**2**, Scheme 1) as prospective, environmentally more friendly alternatives to lead-based compounds, and many other heterocycle-based salts of **2** have been investigated by other groups in the last couple of years.[5,6] We have recently begun to investigate nitrogen-rich salts of the same anion[7] and, in light of the interesting energetic properties of transition metal salts of **2**, were interested to see whether simple s-block (i.e., alkali and alkaline earth) metal salts might also show some useful properties. In the first part of this study, we recently reported the potential of the alkali metal salts of **2** as promising candidates for energetic applications.[8]



Scheme 1. Structural formulas of neutral 5-substituted tetrazoles: 5-amino-1*H*-tetrazole (**1**), 5-nitro-2*H*-tetrazole (**2**), 5-nitriminotetrazole (**3**) and 5-azido-1*H*-tetrazole (**4**).

Sodium 5-nitrotetrazolate dihydrate was first synthesized by von Herz from 5-amino-1*H*-tetrazole (**1**) by treating the insoluble acid copper salt of **2** formed by the diazotization of **1** in the presence of excess nitrite and copper in aqueous solution with excess sodium hydroxide.[9] This sodium salt has subsequently served as a source of the 5-nitro-2*H*-tetrazole moiety in a large number of studies.[9–15] In addition, although many heavy metal salts of **2** have been thoroughly investigated, none of the other alkali or the alkaline earth metal salts of **2** appear to have been particularly well studied[10–12,15–19] until our recent report on the alkali metal salts.[8] We therefore decided to undertake the synthesis and (analytical and spectroscopic) characterization of alkaline

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[a] Department of Chemistry and Biochemistry, Energetic Materials Research, Ludwig Maximilian University
Butenandstr. 5–13, 81377 Munich
Fax: +49-89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

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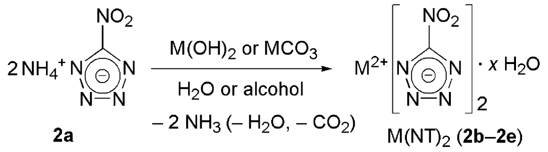
earth metal salts of **2** and study their potential as energetic compounds as a second part of our studies on energetic metal salts of **2**.

Results and Discussion

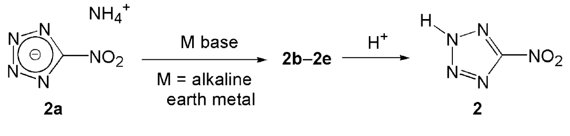
Synthesis

5-Amino-1*H*-tetrazole (**1**) was diazonated with nitrous acid (generated in situ) in the presence of copper(II) sulfate to give the highly sensitive turquoise copper salt. Digestion of this highly insoluble copper salt with sodium hydroxide and removal of black copper(II) oxide by filtration yielded sodium 5-nitrotetrazolate, which was treated in situ with acid, extracted with ethyl acetate[20] and treated with ammonia to precipitate ammonium 5-nitrotetrazolate (**2a**). This compound was subsequently deprotonated with a suitable metal hydroxide or carbonate in alcoholic or aqueous solution, with concomitant formation of ammonia and/or carbon dioxide, to yield the desired 5-nitrotetrazolate (NT^-) salt (Scheme 2). Compounds **2b**–**2e** are obtained as polyhydrates, in analogy to some alkali metal salts of the same anion[8] and to metal salts of the 5,5′-azobis(tetrazolate) anion $[N_4C–N=N–CN_4]^{2-}$.[21]



Scheme 2. Synthesis of alkaline earth metal salts of 5-nitro-2*H*-tetrazole (**2**). M = Mg (**2b**, *x* = 6), Ca (**2c**, *x* = 6), Sr (**2d**, *x* = 5) and Ba (**2e**, *x* = 5).

In addition to having interesting energetic properties, the alkaline earth metal salts of 5-nitro-2*H*-tetrazole (**2**) are also good intermediates for the synthesis of the free acid **2**.[22] The procedure developed in this work starts with anhydrous ammonium 5-nitrotetrazolate (**2a**), whose treatment with an equivalent amount of a suitable basic alkaline earth salt (hydroxide or carbonate), in water, yields the intermediate alkaline earth metal salt (**2b**–**2e**). This salt can then be protonated with sulfuric or hydrochloric acid to form the free acid **2** (Scheme 3), which can be extracted with diethyl ether. Care must be taken during the isolation process since the compound takes up water with time, therefore all operations in air (e.g., determination of the sensitivity towards friction or shock) must be carried out quickly. Additionally, drying of the compound requires high vacuum, and special care must be taken when using (Schlenk) glass vessels due to the high sensitivity of the material.



Scheme 3. Synthesis of the free acid 5-nitro-2*H*-tetrazole (**2**).

Lastly, the alkaline earth metal salts of **2**, as well as **2** itself, are readily soluble in common polar solvents such as water, alcohol, acetone or acetonitrile, soluble in hot thf, and the metal salts are insoluble in apolar or less polar solvents such as pentane, diethyl ether, dichloromethane or chloroform.

NMR and Vibrational Spectroscopy

The alkaline earth metal salts of 5-nitro-2*H*-tetrazole (**2**) were characterized by spectroscopic methods, especially NMR (^1H, ^{13}C and ^{14}N), IR and Raman spectroscopy. The water of crystallisation is observed in the ^1H NMR spectra ([D$_6$]dmso) of all salts as a broad resonance centered at $\delta \approx 3.4$ ppm and is found at high field with respect to the ring proton in neutral **2** ($\delta = 6.29$ ppm).[22] The ring carbon atoms are observed in the ^{13}C NMR spectrum as very low intensity resonances at $\delta \approx 169.0$ ppm in all metal salts. Note that rather concentrated samples are needed in order to obtain a satisfactory signal/noise ratio. The ^{13}C NMR signals are in agreement with those observed for nitrogen-rich salts of the same anion[7] but at high field with respect to metal salts of the 5,5′-azobis(tetrazolate) anion[21] and at low field with respect to metal salts of 5-amino-1*H*-tetrazole (**1**).[23] The three expected resonances resulting from

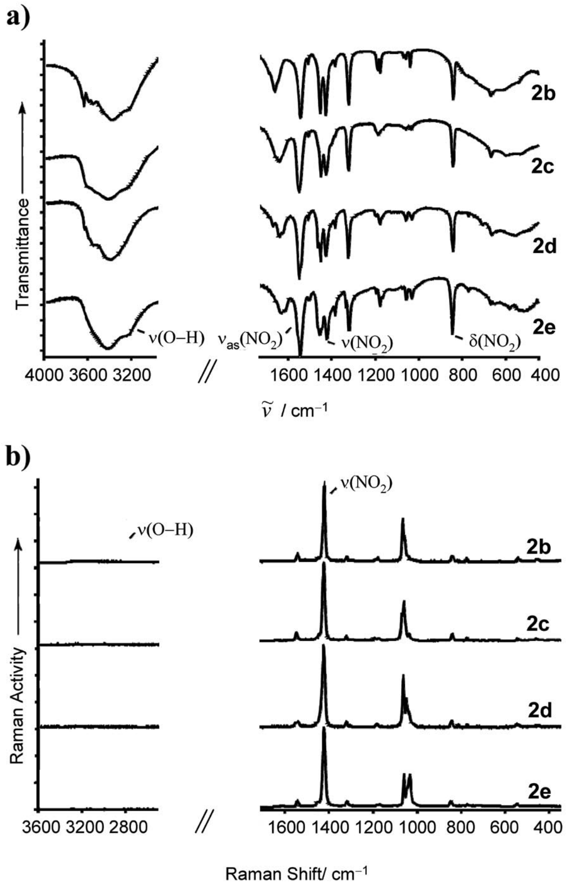


Figure 1. Portions of the IR (a) and Raman (b) spectra of alkaline earth metal salts of 5-nitro-2*H*-tetrazole (**2**).

the high symmetry of the anion can be observed as broad signals in the ^{14}N NMR spectra at $\delta \approx +21$ (N3/N4), –22 (NO_2) and –63 (N2/N5) ppm with $\nu_{1/2} \approx 415$, 60 and 395 Hz, respectively.

The IR and Raman frequencies can be tentatively assigned by comparison with the calculated values.[7] The IR and Raman spectra of the alkaline earth metal salts are shown in Figure 1 for illustration purposes. The three bands which dominate most of the Raman spectra correspond to a coupled (in-phase) NO_2 group and N2–C1–N5 stretching vibration (approx. 1430 cm^{-1}), a coupled N2–C1–N5 deformation and NO_2 group stretching modes (one or two bands at around 1065 cm^{-1}) and to asymmetric deformation vibrations in the ring (approx. 1035 cm^{-1}). These same vibrations appear as one strong and two medium intensity bands in the IR spectra of the compounds at similar wave numbers (approx. 1425, 1060 and 1035 cm^{-1}). Other bands of interest in the IR spectra are the NO_2 group asymmetric stretching mode at around 1545 cm^{-1}, the coupled NO_2 group and N2–C1–N5 (out-of-phase) symmetric stretches at around 1320 cm^{-1} and the coupled NO_2 group and N2–C1–N5 (in-phase) deformation modes at around 845 cm^{-1}.

Crystal Structure of Compound 2c

Single crystals of **2c** were obtained as described in the Experimental Section, and the structure of the compound was determined by X-ray diffraction. Data sets were collected with an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector by using the CrysAlis CCD software.[24] Data reduction was performed with the CrysAlis RED software,[25] the structure was solved by using the corresponding programs available in the WinGX package,[26–29] and the structure was finally checked by using the program PLATON.[30] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were located from difference Fourier electron density maps and refined isotropically. A SCALE3 ABSPACK multi-scan method was used for the absorption correction.[31] Table 1 shows a summary of bond lengths and angles for the two crystallographically independent anions in the structure of compound **2c**. Table 2 summarizes the hydrogen bonds found in the structure, and the distances for the coordination sphere around the Ca^{2+} cations can be found in Table S1 in the Supporting Information.[32]

The two crystallographically independent anions in the structure of compound **2c** have the same geometry as that identified in previous structure determinations of 5-nitrotetrazolate anion (NT^-) containing salts.[6a,7,18,19] The NT^- ring bond lengths (approx. 1.33 Å) are all very similar and comparable to those in other 5-substituted tetrazolate anions with electron-withdrawing substituents,[33] although slightly shorter than those in 5-substituted tetrazolate anions with electron-donating substituents.[23] In addition, the NO_2 group in the two crystallographically independent anions, with N2–C1–N1–O1 and N7–C2–N6–O3 torsion angles of –178.7(2)° and –176.5(2)°, respectively, is essentially coplanar to the ring. This is in contrast to the two crystallographically independent formula units found for the free acid **2** (Figure 2), one of which contains a coplanar NO_2 group [O1–N1–C1–N5 –178.2(3)°], with the other deviating significantly [O3–N6–C2–N10 –164.9(3)°] from the plane formed by the tetrazole ring.[22] A detailed description of the structure of **2c** follows below.

Table 1. Selected interatomic distances and angles for the two crystallographically independent NT^- anions (A and B) in the crystal structure of compound **2c**.

Distances [Å]	**2c** (A)	**2c** (B)	Distances [Å]	**2c** (A)	**2c** (B)
O1–N1	1.236(2)	1.214(2)	C1–N5	1.322(2)	1.318(3)
N1–O2	1.218(2)	1.231(2)	N2–N3	1.332(2)	1.339(2)
N1–C1	1.440(2)	1.439(3)	N3–N4	1.331(2)	1.322(2)
C1–N2	1.317(2)	1.322(3)	N4–N5	1.336(2)	1.337(2)
Angles [°]	**2c (A)**	**2c (B)**	**Angles [°]**	**2c (A)**	**2c (B)**
O1–N1–O2	117.5(2)	116.1(2)	N2–C1–N1	121.6(2)	123.7(2)
O1–N1–C1	124.5(2)	125.4(2)	N3–N4–N5	109.8(1)	108.7(2)
O2–N1–C1	117.9(1)	118.3(2)	C1–N2–N3	103.1(1)	102.6(2)
N2–C1–N5	115.0(2)	114.3(2)	N2–N3–N4	109.4(1)	110.3(2)
N5–C1–N1	123.3(2)	121.9(2)	C1–N5–N4	102.5(1)	103.8(2)

Table 2. Medium to strong hydrogen bonds in the crystal structure of compound **2c**.

D–H···A[a]	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
O5–H52···N9	0.87(4)	2.10(4)	2.937(3)	163(3)
O5–H52···N10	0.87(4)	2.67(4)	3.322(3)	133(3)
O7–H71···N10	0.88(4)	1.92(4)	2.795(3)	170(3)
O8–H82···O4	0.81(5)	2.45(4)	3.021(3)	128(3)
O9–H92···O3	0.75(3)	2.21(3)	2.938(3)	162(3)
O5–H51···N7^{i}	0.84(4)	2.06(4)	2.888(3)	169(3)
O6–H61···N4^{ii}	0.81(4)	2.06(4)	2.830(3)	157(3)
O7–H72···N3^{ii}	0.81(4)	2.06(4)	2.860(3)	170(4)
O6–H62···N2^{iii}	0.80(4)	1.98(4)	2.783(3)	178(4)
O8–H81···N8^{iv}	0.88(4)	1.97(4)	2.846(3)	178(4)
O8–H82···O7^{v}	0.81(5)	2.49(4)	3.171(3)	142(4)
O9–H91···N5^{v}	0.92(4)	2.04(4)	2.941(3)	167(3)
O10–H101···N10^{vi}	0.82(4)	2.47(4)	3.295(3)	177(4)
O10–H102···O6^{vi}	0.92(5)	1.90(5)	2.821(3)	176(4)

[a] Symmetry codes: (i) $-0.5 + x, 1.5 - y, 1 + z$; (ii) $1 - x, 2 - y, -0.5 + z$; (iii) $-x, 2 - y, -0.5 + z$; (iv) $-0.5 + x, 1.5 - y, z$; (v) $+x, y, z$; (vi) $x, y, 1 + z$.

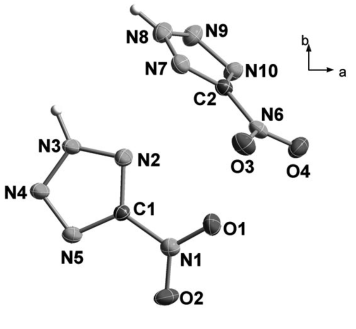


Figure 2. Asymmetric unit of 5-nitro-2*H*-tetrazole (**2**) with the labeling scheme.

Calcium 5-nitrotetrazolate crystallizes as a hexahydrate with all six water molecules found in the coordination sphere of the metal atom and the seventh site being occupied by one of the two anions to form a distorted pentagonal bipyramid (Figure 3). The coordination number around the metal center (CN = 7) is in agreement with a reported average value of 7.31 in calcium salts.[34] Both NT⁻ anions are crystallographically independent, with just one of the anions coordinating to the metal center through one of the two oxygen atoms of the NO_2 group [Ca1–O1 2.554(1) Å]. The other anion is not coordinated and is found at a distance of 4.266(2) Å (Ca1–N10) from the next Ca^{2+} cation. The coordinating anion occupies one of the axial position, forming an angle with the other oxygen atom in the axial position (O1–Ca1–O8) of 153.66(5)°. The water molecules are closely bound to the metal atom with Ca–O distances between 2.352(2) and 2.418(2) Å. The short contacts to the water molecules are in agreement with the high temperature for water loss observed in the DSC measurements (see below).

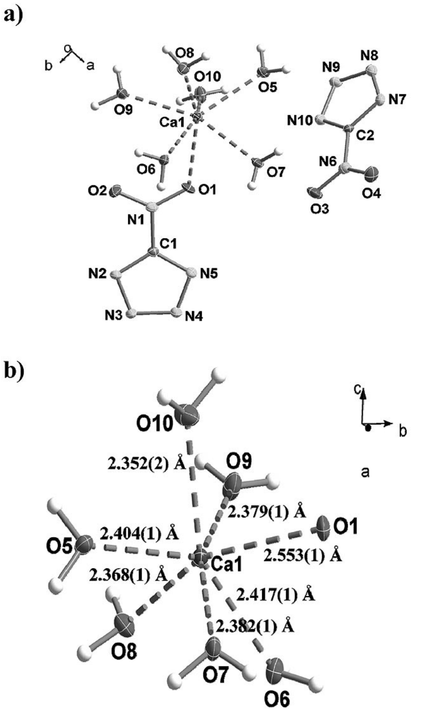


Figure 3. (a) Asymmetric unit of **2c** with the labeling scheme and (b) simplified coordination around the Ca^{2+} cation.

The unit cell of **2c** is represented in Figure 4. The *b*-axis is outstandingly long at 32.575(1) Å, and there is extensive strong hydrogen bonding formed by the water molecules (Table 2), with distances between donor and acceptor atoms in the range 2.8–3.0 Å. At the unitary level, the 14 hydrogen bonds found in the structure describe, exclusively, **D1,1(2)** dimeric patterns, which combine, at the secondary level, to yield finite patterns with the labels **D1,2(3)**, **D2,1(3)** and **D2,2(*X*)** (*X* = 4–7) and **C2,2(*X*)** (*X* = 6, 8) chain networks.[35,36]

Physicochemical Properties

A summary of the physicochemical properties of the metal salts of 5-nitro-2*H*-tetrazole (**2b**–**2e**) can be found in Table 3, which also contains the corresponding values for ammonium 5-nitrotetrazolate (**2a**) for comparison purposes. Differential scanning calorimetry (DSC) measurements were made on samples (approx. 1 mg) of each material in this study and in duplicate. The water of crystallisation in the alkaline earth metal salts is more tightly bound than for the analogous alkali metal salts[8] and is lost at temperatures in the range 100–130 °C (DSC onsets). All alkaline earth metal salts show only a highly exothermic decomposition with concomitant melting and decompose/explode at temperatures in the range 180–235 °C (Table 3). The melting and decomposition points of the salts in this study are generally slightly lower than those observed for metal salts of 5-amino-1*H*-tetrazole (**1**)[23] and 5,5′-azobis(tetrazole).[21] Due to the interest in the use of tetrazole derivatives and their metal salts as energetic materials, a comparison of the energetic properties of the metal salts **2b**–**2e** with those of commonly used explosives is necessary. Once

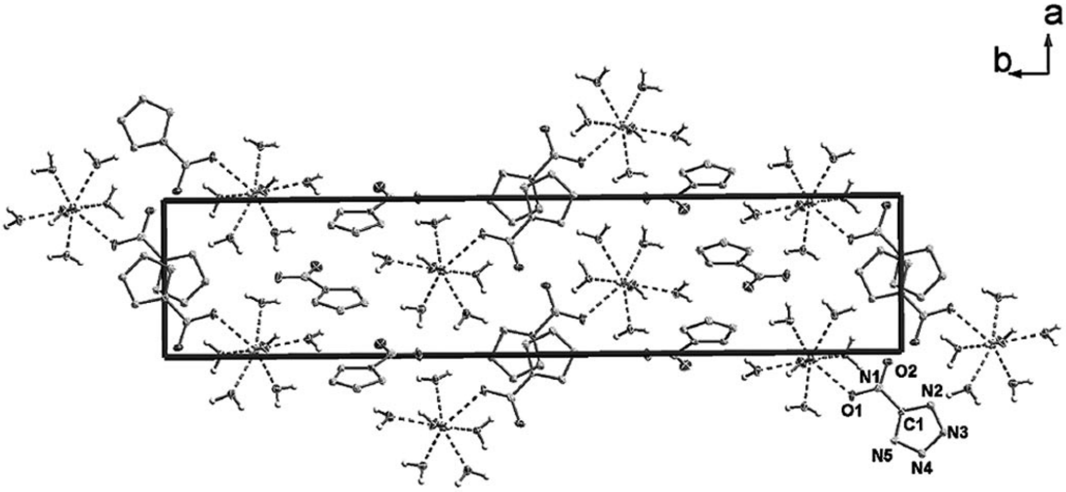


Figure 4. View of the unit cell of **2c** along the *c*-axis (dotted lines depict contacts to the Ca^{2+} cations).

Table 3. Physicochemical properties of alkaline earth metal salts of 5-nitro-2*H*-tetrazole (**2**).

	2a	**2b**	**2c**	**2d**	**2e**
Empirical formula	$C_3H_2N_6O_2$	$C_2H_{12}MgN_{10}O_{10}$	$C_2H_{12}CaN_{10}O_{10}$	$C_2H_{10}N_{10}O_9Sr$	$C_2H_{10}BaN_{10}O_9$
Formula mass [$g\,mol^{-1}$]	154.08	360.48	376.26	405.78	455.49
Impact (*i*) [J][a]	1.5	≥ 40	35	15	2.5–5
Friction (*f*) [N][a]	96	240	84	48	< 20
Electrostatics[b]	–	–	–	–	–
Flame	burns	explodes	explodes	explodes	explodes
N [%][c]	54.5	38.9	37.2	34.5	30.8
N + *O* [%][d]	75.2	83.4	79.7	70.0	62.3
Ω [%][e]	–24.2	–4.4	–4.2	–3.9	–3.5
M.p. [°C][f]	–[g]	119 (– H_2O)	120 (– H_2O)	104 (– H_2O)	129 (– H_2O)
Dec. [°C][f]	210[g]	195	180	210	235

[a] Impact and friction sensitivities determined by standard BAM methods (see refs.[39–41]); the compounds were tested as the crystalline material (**2a**) or as powders (**2b**–**2e**). [b] Rough sensitivity to 20 kV electrostatic discharge (ESD testing): + sensitive, – insensitive from an HF-Vacuum-Tester type VP 24. [c] Nitrogen content. [d] Combined nitrogen and oxygen content. [e] Oxygen balance, calculated according to ref.[42] [f] Melting (or temperature of water loss) and decomposition points (DSC onset) from measurement with β = 5 °C min^{-1}. [g] Taken from ref.[7]

again, all compounds show lower melting and decomposition points than, for example, $Pb(N_3)_2$ and AgN_3.[37] The thermal stability of the salts is greater than that of the free acid 5-nitro-2*H*-tetrazole (**2**), which has a low melting point (below 100 °C) and starts decomposing (highly exothermally) at around 130 °C (DSC onset), similar to 5-azido-1*H*-tetrazole (**4**, Scheme 1).[38] In addition to DSC analysis, all compounds were tested by placing a small sample (approx. 0.5–1 mg) of the compound in a flame. This resulted in a loud explosion in all four cases [both $Pb(N_3)_2$ and AgN_3 explode under similar conditions].

Table 3 also contains the data collected for impact (*i*), friction (*f*) and electrostatic discharge sensitivity testing. The presence of water of crystallisation in compounds **2b**–**2e** means that these compounds are less sensitive than analogous anhydrous salts with alkali metals.[8] Both the impact and friction sensitivities of compounds **2b**–**2e** correlate well with the size of the cation, with the sensitivity increasing in the order Mg < Ca < Sr < Ba. Note also the higher sensitivities of the strontium and barium salts (which contain five molecules of water of crystallisation) in comparison to the hexahydrated magnesium and calcium salts. The sensitivity of the barium salt (**2e**) towards impact (2.5–5.0 J) is very similar to that of lead-based primary explosives such as lead azide (2.5–4.0 J) or lead styphnate (2.5–5.0 J), although the compound is less prone to detonation by a friction stimulus, with a sensitivity value (< 20 N) approximately two times lower than that of lead styphnate (9 N). At the other extreme, the magnesium salt (**2b**) is less sensitive to impact (≥ 40 J) than secondary explosives such as TNT (15 J) and its friction sensitivity (240 N) is halfway between those of TNT (353 N) and the sensitive secondary explosives RDX and HMX (both 120 N).[37] A comparison of these values with those found for 5-nitrotetrazolate salts of nitrogen-rich cations reveals that the compounds in this study are significantly more sensitive to friction and impact.[7] They are also significantly more sensitive than comparable metal salts of **1**[23] and **3**[43,44] (see Scheme 1) but less sensitive than analogous salts of **4**.[45,46] This observation allows us to draw conclusions about the effect of the substituent (R) at the 5-position on the energetic properties of the compounds – the sensitivity of the compounds decreases in the order R = N_3 > NO_2 >> NH-NO_2 > NH_2, which is in good agreement with previous reports.[47a,48] The rough sensitivity of the compounds towards an electrostatic discharge was tested by spraying sparks onto a metal surface containing a few crystals of the corresponding energetic salt by using a tesla coil (ESD testing). In contrast with anhydrous, but in agreement with hydrated, alkali metal salts of the NT^- anion, the compounds reported in this work failed to explode under similar conditions.[8]

Safety Note

Although most of the salts of 5-nitro-2H-tetrazole (**2**) discussed here form as hydrated species and have relatively low sensitivities towards impact and friction, any loss of water of crystallization results in very sensitive materials. Furthermore, the copper salt used in the synthesis of ammonium 5-nitrotetrazolate (**2a**) has been reported to be very sensitive when dry and explodes violently when submitted to an electric discharge,[3,11] therefore it should never be isolated and must always be handled wet. We experienced a large explosion when preparing the barium salt (**2e**). An insoluble solid formed and the explosion was initiated by the action of a magnetic stirrer (see Figure 5a). In a similar

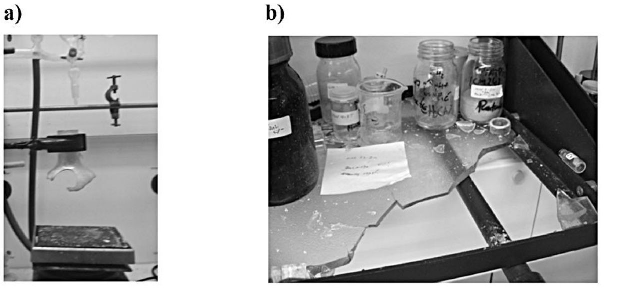


Figure 5. (a) Result of the detonation of barium salt **2e** and (b) strontium salt **2d**.

manner, the strontium salt (**2d**) exploded spontaneously after losing its water of crystallization due to the action of sunlight, destroying a 1-cm thick glass shelf (see Figure 5b).

Conclusions

Alkaline earth metal salts with the energetic 5-nitrotetrazolate anion have been synthesized and characterized by analytical and spectroscopic methods. The calcium salt has also been structurally characterized by single-crystal X-ray diffraction. DSC analysis show good thermal stabilities up to (at least) 180 °C. Standard tests were used to assess the sensitivity of the materials to classical stimuli. All alkaline earth metal salts contain water of crystallisation, which is reflected in the lower sensitivity of these compounds towards shock and friction than anhydrous alkali metal salts containing the same anion. The compounds described here have potential use as energetic materials.

Experimental Section

Caution! Tetrazoles and their derivatives are highly endothermic compounds that tend to release their energy after a given stimulus with the possibility of causing serious damage to their surroundings. The use of safety equipment such as leather gloves, face shield, ear plugs and the use of Teflon spatulas is mandatory. For obvious safety reasons (see Safety Note), the reaction scale should never exceed 250 mg of product!

General: See Supporting Information.

Synthesis of Ammonium 5-Nitrotetrazolate (2a): This compound was synthesized from 5-amino-1*H*-tetrazole, according to a recently published procedure[20] in an overall 52% yield. $CH_4N_6O_2$ (132.04): calcd. C 9.09, H 3.05, N 63.63; found C 8.97, H 3.06, N 63.41. DSC (5 °C min^{-1}): 209 °C (dec.).

Synthesis of Magnesium 5-Nitrotetrazolate Hexahydrate (2b): Ammonium 5-nitrotetrazolate (0.314 g, 2.38 mmol) was dissolved in water (10 mL) and treated with magnesium hydroxide (0.069 g, 1.19 mmol). The reaction mixture was heated at reflux overnight, and the initial suspension became clear with a small amount of insoluble solid. The solution was filtered hot through a folded paper, and the solvent was allowed to slowly evaporate to dryness in a plastic beaker. The dry solid was then carefully removed (*plastic spatula!*) from the beaker and weighed (0.411 g, 96%). The elemental analysis agrees with that of the compound containing six molecules of water. $C_2H_{12}MgN_{10}O_{10}$ (360.48): calcd. C 6.66, H 3.36, N 38.85; found C 6.49, H 3.36, N 38.73. DSC (5 °C min^{-1}): 119 °C (– H_2O), ca. 195 (dec.). MS (FAB$^-$, xenon, 6 keV, *m*-NBA matrix): *m*/*z* = 114.0 [NT]$^-$. ^1H NMR ([D$_6$]dmso, 400.18 MHz, 25 °C, tms): δ = 3.53 (s, H_2O) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]dmso, 100.63 MHz, 25 °C, tms): δ = 168.8 (CNO_2) ppm. ^{14}N NMR ([D$_6$]dmso, 28.89 MHz, 25 °C, tms): δ = +23 ($\nu_{1/2} \approx$ 415 Hz, 2 N, N3/4), –23 ($\nu_{1/2} \approx$ 65 Hz, 1 N, NO_2), –61 ($\nu_{1/2} \approx$ 400 Hz, 2 N, N2/5) ppm. Raman: $\tilde{\nu}$ (%) = 1545 (10), 1424 (100), 1321 (7), 1179 (5), 1066 (52), 1057 (31), 1028 (22), 842 (8), 817 (2), 775 (4), 627 (2), 543 (5), 455 (3), 251 (5) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3633 (s), 3588 (s), 3546 (s), 3379 (s), 2852 (w), 2739 (w), 2476 (w), 2242 (w), 2104 (w), 1873 (w), 1662 (w), 1543 (s), 1507 (w), 1452 (s), 1427 (s), 1384 (w), 1321 (s), 1189 (w), 1178 (w), 1070 (w), 1060 (m), 1040 (m), 843 (m), 671 (m) cm^{-1}.

Synthesis of Calcium 5-Nitrotetrazolate Hexahydrate (2c): Calcium hydroxide (0.072 g, 0.97 mmol) was suspended in ethanol (10 mL) and treated with anhydrous ammonium 5-nitrotetrazolate (0.257 g, 1.95 mmol). The suspension was heated at reflux overnight and filtered hot into a plastic beaker. The solvent was allowed to evaporate, and the solid formed was carefully removed (*plastic spatula!*) onto a piece of paper. No further purification was needed (0.377 g, 93%). Crystals of **2c** suitable for X-ray structure determination were grown by slow concentration of a dilute solution of the compound in ethyl acetate. $C_2H_{12}CaN_{10}O_{10}$ (376.26): calcd. C 6.38, H 3.21, N 37.23; found C 6.50, H 3.19, N 36.94. DSC (5 °C min^{-1}): 120 °C (– H_2O), ca. 180 (dec.) ppm. MS (FAB$^-$, xenon, 6 keV, *m*-NBA matrix): *m*/*z* = 114.0 [NT]$^-$. ^1H NMR ([D$_6$]dmso, 400.18 MHz, 25 °C, tms): δ = 3.43 (s, H_2O) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]dmso, 100.63 MHz, 25 °C, tms): δ = 169.2 (CNO_2) ppm. ^{14}N NMR ([D$_6$]dmso, 28.89 MHz, 25 °C, tms): δ = +20 ($\nu_{1/2} \approx$ 410 Hz, 2 N, N3/4), –22 ($\nu_{1/2} \approx$ 60 Hz, 1 N, NO_2), –65 ($\nu_{1/2} \approx$ 390 Hz, 2 N, N2/5) ppm. Raman: $\tilde{\nu}$ (%) = 1550 (14), 1426 (100), 1323 (10), 1195 (8), 1070 (38), 1062 (52), 1038 (13), 842 (12), 774 (8), 547 (7), 460 (7), 266 (8) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3407 (vs), 2480 (w), 2237 (w), 1643 (m), 1549 (vs), 1507 (w), 1448 (s), 1426 (s), 1322 (s), 1189 (w), 1062 (m), 1037 (m), 842 (s), 669 (m), 594 (m) cm^{-1}.

Synthesis of Strontium 5-Nitrotetrazolate Pentahydrate (2d): A solution of ammonium 5-nitrotetrazolate (0.265 g, 2.01 mmol) in ethanol (10 mL) was heated with strontium hydroxide octahydrate (0.267 g, 1.00 mmol) at reflux overnight. The solution was filtered while still hot, and the solvent was allowed to slowly evaporate in a plastic shell to leave behind a solid compound, which was found to be pure by elemental analysis (0.487 g, 95%). $C_2H_{10}N_{10}O_9Sr$ (405.78): calcd. C 5.92, H 2.48, N 34.52; found C 6.13, H 2.55, N 34.76. DSC (5 °C min^{-1}): 104 °C (– H_2O), ca. 210 (dec.) ppm. MS (FAB$^-$, xenon, 6 keV, *m*-NBA matrix): *m*/*z* = 114.0 [NT]$^-$, 429.7 [Sr(NT)$_3$]$^-$. ^1H NMR ([D$_6$]dmso, 400.18 MHz, 25 °C, tms): δ = 3.37 (s, H_2O) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]dmso, 100.63 MHz, 25 °C, tms): δ = 169.3 (CNO_2) ppm. ^{14}N NMR ([D$_6$]dmso, 28.89 MHz, 25 °C, tms): δ = +21 ($\nu_{1/2} \approx$ 420 Hz, 2 N, N3/4), –22 ($\nu_{1/2} \approx$ 60 Hz, 1 N, NO_2), –63 ($\nu_{1/2} \approx$ 400 Hz, 2 N, N2/5) ppm. Raman: $\tilde{\nu}$ (%) = 3400–2800 (2), 1554 (11), 1432 (100), 1325 (13), 1064 (48), 1039 (37), 848 (16), 774 (4), 551 (5), 278 (3) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3421 (s), 2856 (w), 2465 (w), 2067 (w), 1883 (w), 1630 (m), 1548 (vs), 1505 (m), 1471 (s), 1454 (s), 1426 (s), 1322 (s), 1183 (m), 1062 (m), 1033 (w), 846 (s), 665 (m), 569 (s) cm^{-1}.

Synthesis of Barium 5-Nitrotetrazolate Pentahydrate (2e): Barium hydroxide octahydrate (0.167 g, 0.53 mmol) was suspended in ethanol (5 mL) and treated with a solution of ammonium 5-nitrotetrazolate (0.140 g, 1.06 mmol) in ethanol (5 mL) at reflux overnight. The insoluble solid was then filtered and discarded, and the solution was left to stand to yield the pure compound as a white powder (0.179 g, 93%). $C_2H_{10}BaN_{10}O_9$ (455.49): calcd. C 5.27, H 2.21, N 30.75; found C 5.47, H 2.33, N 30.53. DSC (5 °C min^{-1}): 129, 145 °C (– H_2O), ca. 235 (dec.) ppm. MS (FAB$^-$, xenon, 6 keV, *m*-NBA matrix): *m*/*z* = 114.0 [NT]$^-$, 479.5 [Ba(NT)$_3$]$^-$. ^1H NMR ([D$_6$]dmso, 400.18 MHz, 25 °C, tms): δ = 3.33 (s, H_2O) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]dmso, 100.63 MHz, 25 °C, tms): δ = 168.7 (CNO_2) ppm. ^{14}N NMR ([D$_6$]dmso, 28.89 MHz, 25 °C, tms): δ = +20 ($\nu_{1/2}$ $\approx$ 420 Hz, 2 N, N3/4), –22 ($\nu_{1/2} \approx$ 60 Hz, 1 N, NO_2), –64 ($\nu_{1/2} \approx$ 390 Hz, 2 N, N2/5) ppm. Raman: $\tilde{\nu}$ (%) = 3300–2900 (2), 1544 (10), 1425 (100), 1322 (9), 1173 (2), 1061 (47), 1038 (35), 845 (8), 774 (6), 546 (5), 410 (3), 251 (3), 147 (3) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3221 (vs), 2962 (s), 2923 (s), 2849 (m), 2739 (w), 2456 (w), 2190 (w), 2058 (w), 1876 (w), 1686 (vs), 1629 (s), 1546 (vs), 1504 (m), 1451 (s), 1424 (s), 1378 (m), 1319 (s), 1179 (s), 1152 (m), 1129 (m), 1060 (s), 1033 (m), 951 (s), 884 (vs), 845 (m), 772 (m), 665 (m), 638 (m), 534 (m) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Geometric parameters for the coordination around the cation in salt 2c and the general experimental method.

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