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PAPER

Metal salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion ($[C_4N_5]^-$)†

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Diaminomaleodinitrile was reacted at low temperatures with *in situ* generated nitrous acid to form 4,5-dicyano-2*H*-1,2,3-triazole (**1**) in yields above 90%. Crystalline **1** was then reacted with one equivalent of a suitable alkali or alkaline earth metal base (typically a hydroxide or a carbonate) in a polar solvent to form the corresponding alkali and alkaline earth metal salts of 4,5-dicyano-2*H*-1,2,3-triazole (compounds **2–9**). The thermal stability of the metal salts **2–9** was assessed by differential scanning calorimetry, which showed excellent thermal stabilities up to above 350 °C. Due to the energetic character of triazole-based salts, initial safety testing was used to assess the sensitivity of compounds **2–9** towards impact, friction, electrostatic discharge and fast heating. These results revealed very low sensitivities towards all four stimuli. Additionally, compounds **2–9** were characterized by mass spectrometry, elemental analysis, infrared and Raman spectroscopy and (^1H, ^{13}C and ^{14}N) NMR spectroscopy. We also determined the solid state structure of the 4,5-dicyano-2*H*-1,2,3-triazole anion of one of the alkali metal salts (**4**: Monoclinic, $P2_1/c$, $a = 9.389(1)$ Å, $b = 10.603(1)$ Å, $c = 6.924(1)$ Å, $\beta = 102.75(1)°$ and $V = 1036.58(3)$ Å^3) and one of the alkaline earth metal salts (**6**: Monoclinic, $P2_1/c$, $a = 9.243(1)$ Å, $b = 15.828(2)$ Å, $c = 6.463(1)$ Å, $\beta = 90.23(1)°$ and $V = 945.5(2)$ Å^3). Furthermore, we noted the hydrolysis of one of the cyano groups of the 4,5-dicyano-2*H*-1,2,3-triazole anion in the strontium salt **8** to form the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid derivative **8b**, as confirmed by X-ray studies (**8b**: Monoclinic, $P2_1/n$, $a = 6.950(1)$ Å, $b = 17.769(1)$ Å, $c = 13.858(1)$ Å, $\beta = 92.98(1)°$ and $V = 1709.1(1)$ Å^3). Lastly, we computed the NBO and Mülliken charges for the anion of compounds **2–9** and those of the anion of compound **8b**.

Introduction

Pyrotechnics are compounds which are generally used to cause an audiovisual effect (*e.g.*, light, smoke, sound, *etc.*) and have a wide variety of applications in the field of fireworks, airbags, fire extinguishers, (road) flares, matches, and production of nanoporous foams and propellants. A classical pyrotechnic formulation is composed of an oxidizer, a reducing agent, (optionally) a binder, a propellant, a sound- or smoke-producing agent and a colouring agent.[1] However, many of the commonly used energetic compounds are either toxic or form toxic decomposition products.

In this line, nitrogen-rich compounds were investigated for application in the field of gas generators,[2–4] blowing agents,[3–5] primary explosives[5] and as ingredients in pyrotechnic and propellant mixtures.[6] Nitrogen-rich compounds have received considerable attention due to the fact that dinitrogen formation upon combustion leads to very negative enthalpies of combustion, *i.e.*, very positive heats of formation. A prominent type of nitrogen-rich energetic compound which has been widely studied is azole-based energetic materials.[7,8] These materials contain N–N bonds in the ring, which are stabilized by aromaticity and show relatively low sensitivities and high thermal stabilities.

The heats of formation of azoles (Fig. 1) increase in the direction 1*H*-pyrrole (**A**) to 3*H*-pentazole (**G**), in agreement with an increase in the nitrogen content. Not surprisingly, the stability decreases in the same direction. Triazole- and tetrazole-based

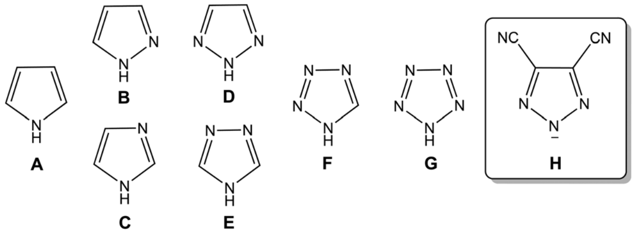

Fig. 1 Formula structure of unsubstituted neutral azoles: **A** = 1*H*-pyrrole, **B** = 1*H*-pyrazole, **C** = 1*H*-imidazole, **D** = 2*H*-1,2,3-triazole, **E** = 4*H*-1,2,4-triazole, **F** = 1*H*-tetrazole, **G** = 3*H*-pentazole and **H** = 4,5-dicyano-2*H*-1,2,3-triazole anion.

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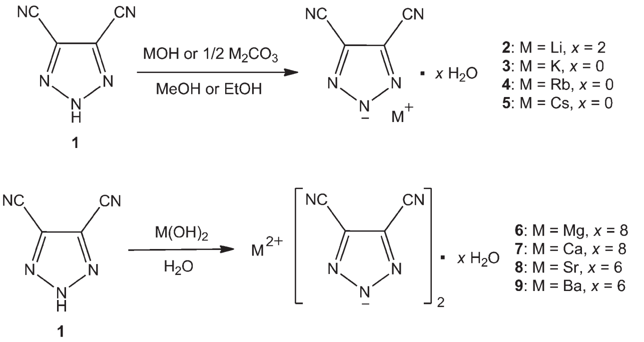
† Electronic supplementary information (ESI) available: General method, calculated IR/Raman frequencies, X-ray tables for compounds **4**, **6** and **8b** and graph-set analysis of compounds **6** and **8b**. CCDC reference numbers 852499–852501. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12100j

energetic materials seem to exhibit the best compromise between high energy content and good chemical and thermal stability and in the last few years they have been investigated for application as propellants or secondary explosives.[9,10] Recently, the synthesis of polycyano compounds by Shreeve *et al.*[11] showed that cyano groups can be used to increase the heats of formation (*i.e.*, the energy content) of energetic materials. This work prompted us to study the energetic properties of the sodium, potassium, ammonium, hydrazinium and guanidinium salts of the 5-cyanotetrazole anion ($[C_2N_5]^-$, Fig. 1).[12]

In contrast to tetrazole derivatives, triazole-based energetic materials have been less studied.[13–16] Both possible isomers of triazole, *i.e.*, **D** = 2*H*-1,2,3-triazole and **E** = 4*H*-1,2,4-triazole, are known to have high positive heats of formation of 272 kJ mol^{-1} and 109 kJ mol^{-1}, respectively.[17,18] Therefore, **D** should be of greater interest than **E** for the synthesis of energetic derivatives.

The promising properties of energetic salts of the 5-cyanotetrazole anion,[12] attracted our attention to the parent 4,5-dicyano-2*H*-1,2,3-triazole (**1**). The synthesis of neutral 4,5-dicyano-2*H*-1,2,3-triazole was reported as early as 1921 by the diazotation of aminomalononitrile with *in situ* generated "HNO_2".[19] Shortly after, the same authors described the characterization of the ammonium, potassium, calcium, barium, copper and silver salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion mainly only by solubility and melting point.[19,20] In 2003 and 2004 several groups investigated the lithium salt and characterized it only by Raman spectroscopy.[21] Unfortunately, characterization data of salts of 4,5-dicyano-2*H*-1,2,3-triazole were not reported. The authors of the latter references reported on the relatively non-coordinating behaviour of this anion for use in polymer electrolytes. In addition to the previous studies, a high number of rhodium complexes of this anion were reported[22] and only recently, the synthesis and crystal structure of the first actinide complex of the 4,5-dicyano-2*H*-1,2,3-triazole anion, namely $UO_2((NC)_2C_2N_3)_2(OPPh_3)_3$ was reported by Crawford *et al.*[23]

In addition to the metal salts introduced above, many salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion with nitrogen bases have also been described by Toshiaki *et al.*[24] In 2007, ammonium and imidazolium salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion were described by Mizuta and coworkers as a new class of ionic liquids with potential for electrochemical applications[25] and in 2010, Kitaoka *et al.* described the preparation and properties of imidazolium, pyridinium, and pyrrolidinium salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion.[26] The latter compounds were claimed to be ionic liquids with lower viscosity and glass transition temperature than ionic liquids not containing cyano groups. However, none of the derivatives of 4,5-dicyano-2*H*-1,2,3-triazole described are energetic.[19–26] Recent work by the Klapötke group reported on the synthesis and full characterization (including crystal structure analysis) of 4,5-dicyano-2*H*-1,2,3-triazole and its sodium, silver, ammonium and guanidinium salts.[27] The ammonium and guanidinium salts are highly endothermic and thermally stable energetic compounds. In view of the interesting energetic properties of the recently reported salts of the 5-cyanotetrazole[12] and 4,5-dicyano-2*H*-1,2,3-triazole[27] anions, we became interested to investigate whether the simple alkali and alkaline earth metal salts of 4,5-dicyano-2*H*-1,2,3-triazole might also show some desirable energetic properties. Therefore, here we would like to describe our results on the synthesis, full analytical and spectroscopic characterization, energetic properties and X-ray structures of alkali and alkaline earth metal salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion ($[C_4N_5]^-$) .



Scheme 1 Protocol for the synthesis of 4,5-dicyano-2*H*-1,2,3-triazole (**1**) and its alkali (**2–5**) and alkaline earth (**6–9**) metal salts.

Results and discussion

Synthesis and stability

4,5-Dicyano-2*H*-1,2,3-triazole (**1**) was obtained by a modified literature procedure[21*a*,23] (see Experimental section). Sublimed crystalline **1** was then reacted with one equivalent of a suitable alkali metal hydroxide or carbonate in alcohol or with one equivalent of the corresponding alkaline earth metal hydroxide in water to prepare the alkali metal (compounds **2–5**) and alkaline earth metal (compounds **6–9**) salts of **1** (Scheme 1). The synthesis and characterization of the previously reported sodium salt[23] and of the highly toxic beryllium salt were outside the scope of this study.

Apart from the lithium salt (**2**), which is highly hygroscopic, the remainder of the compounds are stable to moisture and all salts of **1** are chemically and thermally stable over (at least) several months. The alkali metal salts **2–5** are readily soluble in polar solvents such as acetone, alcohol, water or DMSO and insoluble in less polar solvents such as ether or chloroform. On the other hand, the alkaline earth metal salts **6–9** are significantly less soluble and do not dissolve in acetone or alcohol and they are less soluble in water or DMSO. The solubility of compounds **6–9** in water decreases in the direction Mg (**6**) > Ca (**7**) > Sr (**8**) > Ba (**9**) so that whereas the magnesium salt (**6**) is readily soluble at room temperature, the barium derivative (**9**) dissolves only in hot water. Lastly, we found that when a solution of compound **8** in water is heated, hydrolysis of one of the cyano groups takes place forming compound **8b**, which is based on the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anion (see X-ray discussion below).

Due to the endothermic character of 1,2,4-triazole ($\Delta_f H$ = 26.1 kcal mol^{-1})[28] and its salts[8*b*] and of cyano compounds,[11] salts based on the 4,5-dicyano-2*H*-1,2,3-triazole anion are potentially energetic compounds. Therefore, we assessed the energetic properties of compounds **2–9** using standardized test methods. BAM methods[29–34] were used to gain insight into the sensitivity of the compounds in this study towards impact, friction,

Table 1 Physical, chemical and energetic properties of compounds **2–9**

	2	$Na[C_2N_5]\cdot H_2O$	**3**	**4**	**5**
Formula	$C_4H_4N_5O_2Li$	$C_4H_2N_5ONa$	C_4N_5K	C_4N_5Rb	C_4N_5Cs
MW (g mol^{-1})	161.05	159.08	157.17	203.54	250.98
Impact (J)[a]	>40	>40	>40	>40	>40
Friction (N)[a]	>360	>360	>360	>360	>360
Electrostatics (20 kV)[a]	—	—	—	—	—
Flame	Burning	Burning	Burning	Burning	Burning
Flame colour	Red	Orange	Purple	Red	Pink
N (%)[b]	43	44	45	34	28
mp (°C)[c]	—	—	—	—	—
dec (°C)[d]	322	305	314	297	294

	6	**7**	**8**	**9**
Formula	$C_8H_{16}N_{10}O_8Mg$	$C_8H_{16}N_{10}O_8Ca$	$C_8H_{12}N_{10}O_6Sr$	$C_8H_{12}N_{10}O_6Ba$
MW (g mol^{-1})	404.58	420.35	431.86	481.57
Impact (J)[a]	>40	>40	>40	>40
Friction (N)[a]	>360	>360	>360	>360
Electrostatics (20 kV)[a]	—	—	—	—
Flame	Burning	Burning	Burning	Burning
Flame colour	White	Lavender	Red	Green
N (%)[b]	35	33	32	29
mp (°C)[c]	—	—	—	—
dec (°C)[d]	317	308	334	351

[a] Impact friction and electrostatic discharge sensitivities determined by standard BAM methods (see ref. 30–33). [b] Nitrogen content. [c] Melting point (DSC onset) from measurement with $\beta = 5$ °C min^{-1}. [d] Decomposition point (DSC onset) from measurement with $\beta = 5$ °C min^{-1}.

electrostatic discharge and heating. Table 1 contains a summary of physical, chemical and energetic properties of compounds **2–9**. According to our results, compounds **2–9** are impact (>40 J), friction (>360 N) and electrostatics (20 kV) insensitive and therefore classify as safe for transport according to UN recommendations.[34] The low sensitivity of compounds **2–9** is a clear advantage over the high sensitivity of previously reported metal salts of 5-nitro-2*H*-tetrazole.[35]

The thermal stability of compounds **2–9** was assessed by differential scanning calorimetry (DSC). All materials have excellent thermal stabilities (generally) above 300 °C. For the alkali metal salts **2–5** the decomposition temperatures seem to decrease with the size of the cation (*i.e.*, Li (**2**) > K (**3**) > Rb (**4**) > Cs (**5**)) whereas the opposite trend is observed for the alkaline earth metal salts (*i.e.*, Mg (**6**) > Ca (**7**) < Sr (**8**) < Ba (**9**)). The decomposition temperatures of compounds **2–9** are significantly higher than those of previously reported alkali and alkaline earth metal salts with azole-based anions.[35–37]

In addition to DSC analysis, all metal salts of 4,5-dicyano-2*H*-1,2,3-triazole were tested in the "flame test", where a few milligrams of the compound were placed on a metal spatula and the spatula was held in the open flame of a *Bunsen* burner. Fast heating of the alkali metal salts of 4,5-dicyano-2*H*-1,2,3-triazole results in normal burning with little smoke accompanied by the characteristic colour of the metal cation (*i.e.*, red (**2**), purple (**3**), red (**4**) and pink (**5**)) whereas the alkaline earth metal salts burn slightly more vigorously, also giving the corresponding flame colour of the metal centre (*i.e.*, white (**6**), lavender (**7**), red (**8**) and green (**9**)).

Spectroscopic discussion

All salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion were characterized by vibrational spectroscopy (IR and Raman) as well as NMR spectroscopy (^{1}H, ^{13}C and ^{14}N NMR). The B3LYP method was used to facilitate the assignment of the vibrational bands observed in the IR and Raman spectra of compounds **2–9**. We used a 6-31+G(d,p) basis set to predict the (gas phase) vibrational frequencies of the 4,5-dicyano-2*H*-1,2,3-triazole anion (see Experimental part for details on the computational method used). The supporting information (Table 1, ESI†) contains a summary of the (scaled) predicted vibrational frequencies of the 4,5-dicyano-2*H*-1,2,3-triazole anion with the corresponding IR intensities and Raman activities and averaged experimental values. The most intense band observed in both IR and Raman spectra of salts **2–9** corresponds to the stretching vibrations of the two cyano groups (strong band at *ca.* 2250 cm^{-1} (ν_s(C≡N)) with a shoulder at *ca.* 2240 cm^{-1} (ν_{as}(C≡N))). The remainder of the bands are of lower intensity/activity and can be assigned as follows: 1505–1090 cm^{-1} (ring C–N and N–N stretching modes), 1010–710 cm^{-1} (ring N–N–N bending vibrations), 660–430 cm^{-1} (ring N–C–C and N–N–C bending modes) and 605–430 cm^{-1} (C–C≡N bending vibrations).

Due to the lack of hydrogen atoms, the ^{1}H NMR spectra of the salts of the 4,5-dicyano-2*H*-1,2,3-triazole anion only show the resonances corresponding to the protons of the solvated water molecules at $\delta \sim 3.4$ ppm. On the other hand, the ^{13}C NMR spectra show two resonances at $\delta \sim 121.0$ and $\delta \sim 114.0$ ppm, corresponding to the cyano groups and triazole ring, respectively. Additionally, the ^{14}N NMR spectra are characterized by broad bands at $\delta \sim +25$ ($\nu_{1/2} = 700$ Hz, N5), -25 ($\nu_{1/2} = 800$ Hz, N4–N6) and -120 ($\nu_{1/2} = 700$ Hz, N1–N9) ppm.

X-ray crystal structures

The 4,5-dicyano-1,2,3-triazole anions in the solid state structure of the rubidium salt **4** and the magnesium salt **6** (Tables 2 and 3) do not show significant differences. A similar situation is found for the two crystallographically independent anions **8b (1)** and **8b (2)** in the crystal structure of the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid salt **8b** (for labelling schemes see Fig. 2). For all three compounds **4**, **6** and **8b**, the N–N distances of the triazole ring, in the range between *ca.* 1.33 and 1.36 Å, are between typical N–N single (1.454 Å) and N═N double bonds (1.245 Å).[38] The cyano group C–N distances (*ca.* 1.14–1.15 Å) are comparable to those of recently reported salts of 5-cyanotetrazole[12] and 4,5-dicyano-1,2,3-triazole.[27] The remainder of the C–N distances, in the range between *ca.* 1.33 and 1.35 Å are also shorter than the average C–N single bond distance (1.47 Å)[39] and point at a highly delocalized electronic system.

The rubidium salt **4** crystallizes in a monoclinic cell of the space group $P2_1/c$. The asymmetric unit of the compound is made up of one crystallographically independent Rb^{+} cation and one 4,5-dicyano-2*H*-1,2,3-triazole anion. All nitrogen atoms of the anion are involved in coordination to the metal centre (Fig. 3a) with Rb–N distances in the range 2.93–3.27 Å, comparable to those previously found in rubidium 5-nitrotetrazolate.[35] The coordination around the rubidium atoms is completed by interaction to seven anions (Fig. 3b) accounting for a coordination number of nine. This coordination mode is usual for rubidium salts.[16,40]

The 4,5-dicyano-2*H*-1,2,3-triazole anions and rubidium cations form planar layers perpendicular to the *ac*-plane, which are connected among them by the Rb–N contacts discussed above (Fig. 4a). Additionally, the layers of anions form infinite chains along the *c*-axis with each layer twisted by approximately 180° with respect to the previous one (Fig. 4b).

Table 2 Selected bond distances (Å) found experimentally for the 4,5-dicyano-2*H*-1,2,3-triazole and the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anions

	4	6	8b (1)	8b (2)
N1–C2	1.151(4)	1.144(7)	1.150(6)	1.145(7)
C2–C3	1.423(4)	1.434(7)	1.424(6)	1.424(7)
C3–N4	1.352(4)	1.325(6)	1.337(6)	1.349(5)
C3–C7	1.387(4)	1.386(7)	1.380(6)	1.394(6)
N4–N5	1.341(3)	1.328(5)	1.337(5)	1.339(5)
N5–N6	1.355(4)	1.325(5)	1.329(5)	1.342(5)
N6–C7	1.333(4)	1.329(6)	1.344(5)	1.342(6)
C7–C8	1.432(4)	1.421(6)	1.488(6)	1.476(6)
C8–N9	1.143(4)	1.139(6)		
C8–O9			1.326(5)	1.331(6)
C8–O10			1.237(5)	1.233(6)

In analogy to the rubidium salt **4**, the magnesium salt **6** also crystallizes in a monoclinic cell of the space group $P2_1/c$. In the crystal structure of **6** the Mg^{2+} cations sit on a symmetry plane with half of the solvated water molecules and half of the anions being generated by symmetry (symmetry code: (i) $2 - x$, $1 - y$, $2 - z$). The asymmetric unit is made up of one Mg^{2+} cation, one 4,5-dicyano-2*H*-1,2,3-triazole anion and four molecules of water so that the overall charge is zero and, therefore, the compound is an octahydrate. Fig. 5 shows a view of the unit cell of the salt **6**. The coordination around the metal centre is completed by interaction to six solvated water molecules (two times three crystallographically independent molecules) with distances between Mg and O atoms varying within a narrow range (2.05 to 2.07 Å) and angles close to the ideal 90 and 180° expected for a regular octahedron. The octahedral geometry is common for magnesium salts containing a nitrogen-rich anion.[37b] The fourth molecule of water (O13) is not involved in coordination to the metal centre but in hydrogen-bonding (see discussion below). The Mg^{2+} cations occupy the middle points of the vertices of the two faces on the *bc*-plane with the 4,5-dicyano-2*H*-1,2,3-triazole anions filling the unit cell. All nitrogen atoms in the anions are involved in hydrogen-bonding to water molecules *via* five out of the seven hydrogen bonds found in the structure of the compound. The remainder of the hydrogen bonds are formed by interaction between two solvated water molecules.

Recrystallization of compound **8** from hot water resulted in hydrolysis of one of the cyano groups to form the strontium salt

Table 3 Selected bond angles (°) found experimentally for the 4,5-dicyano-2*H*-1,2,3-triazole and the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anions

	4	6	8b (1)	8b (2)
N1–C2–C3	178.7(3)	178.0(6)	176.7(5)	177.6(5)
C2–C3–N4	122.5(3)	123.7(4)	121.3(4)	122.2(4)
C2–C3–C7	130.0(3)	128.7(4)	130.2(4)	128.9(4)
N4–C3–C7	107.5(3)	107.5(4)	108.2(4)	108.8(4)
C3–N4–N5	106.2(2)	107.1(4)	106.5(4)	105.7(4)
N4–N5–N6	112.1(2)	110.9(4)	110.9(3)	111.5(4)
N5–N6–C7	105.9(2)	107.0(4)	107.0(3)	107.3(4)
C3–C7–N6	108.2(3)	107.5(4)	107.3(4)	106.7(4)
C3–C7–C8	130.2(3)	128.0(4)	127.7(4)	127.0(4)
N6–C7–C8	121.6(3)	124.5(4)	125.0(4)	126.2(4)
C7–C8–N9	179.6(3)	175.9(6)		
C7–C8–O9			117.4(4)	118.2(4)
C7–C8–O10			118.2(4)	118.4(4)
O9–C8–O10			124.4(4)	123.4(4)

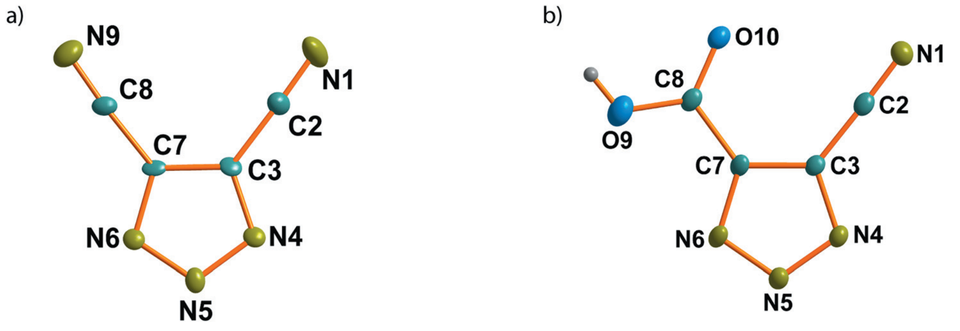


Fig. 2 Labelling schemes for the 4,5-dicyano-1,2,3-triazole anion (a) and the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anion (b).

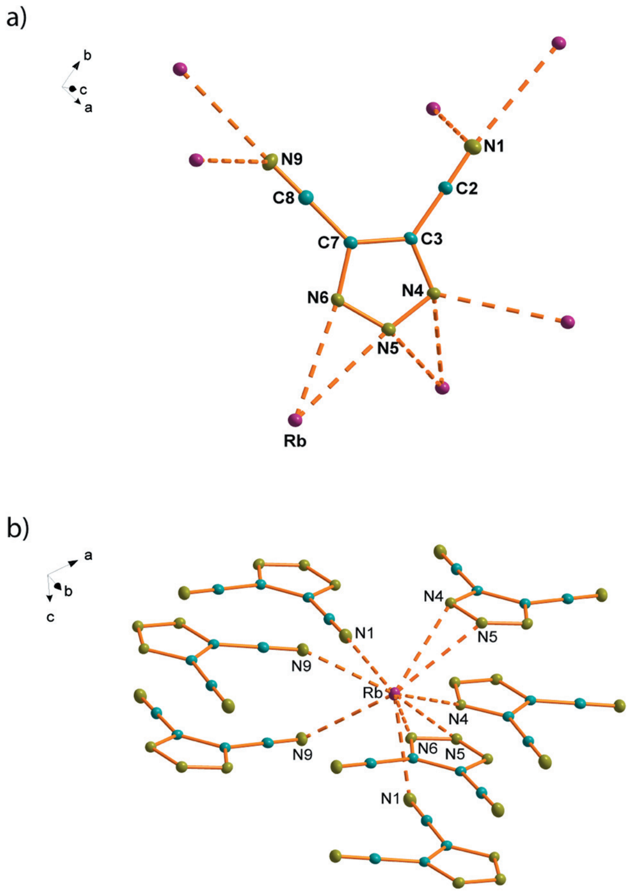


Fig. 3 Labelling scheme and packing around the anion (a) and cation (b) in the crystal structure of compound **4** (diamond ellipsoids represented at 50% probability). Dotted lines represent Rb–N coordination.

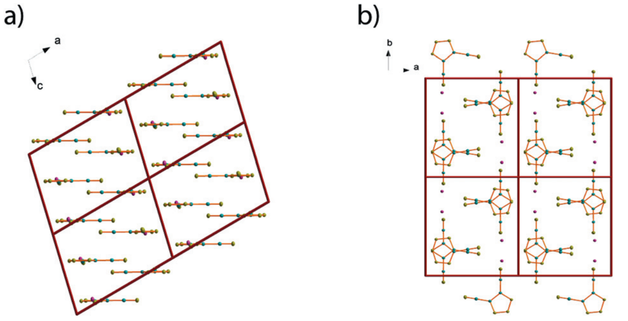


Fig. 4 View of the 2 × 2 × 2 supercell along the *b*-axis (a) and along the *c*-axis (b) in the crystal structure of compound **4**. The Rb–N coordination has been omitted for clarity purposes.

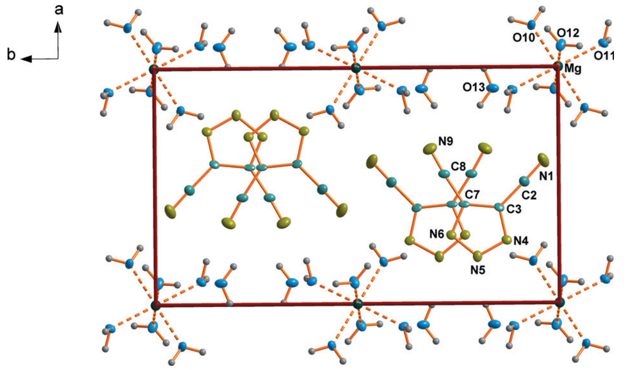
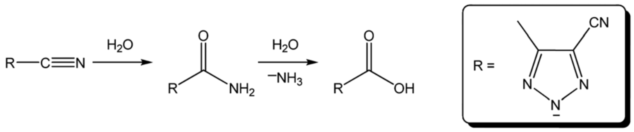


Fig. 5 Unit cell of compound **6** (view along the *c*-axis) showing the coordination around the Mg^{2+} cations (dotted lines) and the labelling scheme.



Scheme 2 Proposed mechanism for the hydrolysis of the 4,5-dicyano-2*H*-1,2,3-triazole salt **8** to the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid derivative **8b**.

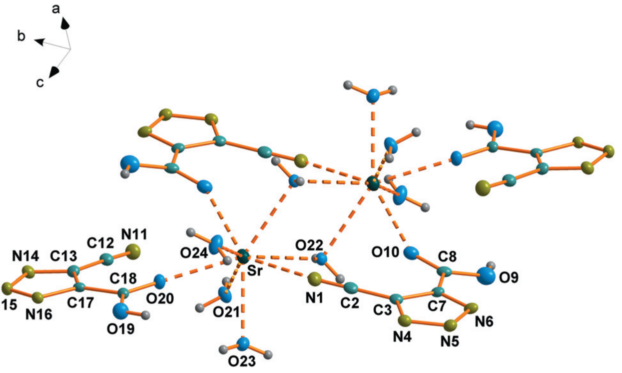


Fig. 6 Packing around the Sr^{2+} cation in the crystal structure of compound **8b** and labelling scheme (diamond ellipsoids represented at 50% probability). Dotted lines represent Sr–N and Sr–O coordination.

8b. The proposed mechanism for the hydrolysis of one of the cyano groups to form salt **8b** is depicted in Scheme 2. Note that the anion of compound **8b** holds a proton on the carboxylic group whereas the triazole ring is deprotonated. This can be explained by the high delocalization of the triazole ring negative charge in salt **8b** around the ring and over to the cyano and carboxylic acid groups. This delocalization increases the acidity of the triazole proton in comparison to the carboxylic acid proton in 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid. The unusually high acidity of the triazole ring was already noticed in preliminary tests when trying to protonate 4,5-dicyano-2*H*-1,2,3-triazole (**1**) to form the corresponding chloride and picrate salts. When ether solutions of **1** were reacted with ether solutions of hydrochloric or picric acid, no precipitation of the expected chloride and picrate salts was observed and only unreacted **1** was recovered.

Compound **8b** crystallizes in a monoclinic cell in the space group $P2_1/n$. The asymmetric unit is made up of one Sr^{2+} cation, two 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anions and four solvated water molecules. Note the existence of a longer and a shorter C–O bond (C–O ~1.33 Å and C–O ~1.23 Å, respectively). The coordination number around the Sr^{2+} cations is eight (Fig. 6). Only one of the two oxygen atoms in the anion is involved in the coordination around the metal centre with Sr–O distances in the range 2.48–2.54 Å. Additionally, the four water molecules are involved in three short coordination bonds (2.55–2.58 Å) and two longer contacts (2.71–2.73 Å). Lastly, only the nitrogen atom of the –CN group is involved in coordination (Sr–N ~2.73 Å), whereas the remainder of nitrogen atoms are involved in hydrogen-bonding. As represented in Fig. 6, two asymmetric units, *i.e.*, $SrA_2 \cdot 4H_2O$ (A = 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anion) are bridged by the two longer contacts to water molecules described above to form $[Sr_2A_4 \cdot 8H_2O]$ clusters. These "dimeric" clusters are connected to other clusters in the structure through hydrogen-bonding.

Table 4 Crystal data and structure refinements for compounds **4**, **6** and **8b**

Parameter	**4**	**6**	**8b**
CCDC N°	852499	852500	852501
Empirical formula	C_4N_5Rb	$C_8H_{16}N_{10}O_8Mg$	$C_8H_8N_8O_8Sr$
Formula weight [g mol^{-1}]	203.54	404.62	431.81
Habit	Block	Needle	Needle
Colour	Colourless	Colourless	Colourless
Temperature/K	100	100	100
Crystal size/mm^3	0.363 × 0.200 × 0.172	0.655 × 0.200 × 0.123	0.458 × 0.182 × 0.123
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	9.389(1)	9.243(1)	6.950(1)
b/Å	10.603(1)	15.828(2)	17.769(1)
c/Å	6.924(1)	6.463(1)	13.858(1)
α (°)	90.00	90	90.00
β (°)	102.75(1)	90.23(1)	92.98(1)
γ (°)	90.00	90	90.00
V_{UC}/Å^3	1036.58(3)	945.5(2)	1709.1(1)
Z	4	2	4
ρ_{calc}/g cm^{-3}	2.011	1.421	1.662
μ/mm^{-1}	7.285	0.153	3.210
F (000)	384	420	864
θ range (°)	3.57–29.36	3.40–29.42	3.41–29.54
Index ranges	$-12 \le h \le 12$ $-14 \le k \le 14$ $-9 \le l \le 9$	$-12 \le h \le 12$ $0 \le k \le 21$ $0 \le l \le 8$	$-9 \le h \le 9$ $0 \le k \le 24$ $0 \le l \le 19$
Reflections collected	3722	5266	9560
Independent reflections	1715	2361	4505
Data/restraints/parameters	1715/0/92	2361/0/125	4505/0/226
Goodness-of-fit on F^2	0.955	1.053	0.954
R_{int}	0.051	0.080	0.068
R_1 [$F > 4\sigma(F)$]	0.030	0.097	0.057
R_1 (all data)	0.034	0.106	0.071
wR_2 [$F > 4\sigma(F)$]	0.071	0.173	0.121
wR_2 (all data)	0.075	0.175	0.136

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

Experimental section

Cautionary note

Although initial safety testing indicated that compounds **2–9** have low sensitivities against classical stimuli, they ought to be regarded as potentially explosive materials and adequate safety practice is recommended at all times. The synthesis of these compounds ought to be only carried out by trained personnel using appropriate safety equipment.

X-ray crystal structure determination

The crystallographic data for compounds **4**, **6** and **8b** (Table 4) was collected using an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector. The CrysAlis Pro software[41] was used for the data collection and reduction and the structure was solved using the WinGX software.[42,43] The non-hydrogen atoms were refined anisotropically and a multi-scan absorption correction was applied.[44] Tables 2–5 of the ESI† contain a summary of the metal–nitrogen and metal–oxygen distances and angles and the geometry of the hydrogen bonds in compounds **4**, **6** and **8b**.

Computational section

The gas phase geometry of the 4,5-dicyano-2*H*-1,2,3-triazole anion was optimized using DFT calculations (B3LYP/6-311+G(d,p)).[45,46] No imaginary frequencies were found and the optimized structure was a true minimum on the potential energy surface. The optimized structure of the 4,5-dicyano-1,2,3-triazolate anion was then used to compute the harmonic vibrational frequencies, the infrared intensities and the Raman activities using Gaussian 03W.[47] The computed frequencies were scaled by a factor of 0.9613.[48]

4,5-Dicyano-2*H*-1,2,3-triazole (1). **1** was synthesized by the following modified literature procedure:[27,49] 98% diaminomaleodinitrile (10.81 g, 98.00 mmol) was dissolved in 1 N hydrochloric acid (100 mL) and cooled to 0 °C. A solution of sodium nitrite (6.89 g, 100.0 mmol) in distilled water (125 mL) was added to the above solution taking care that the temperature in the reaction flask did not exceed 5 °C. After stirring for 30 min in the cold, the reaction mixture was allowed to reach room temperature and was further stirred for 1 h. The dark brown solution that had formed was filtered and the insoluble materials were washed with water. The filtrates were extracted with diethyl ether (6 × 100 mL) and the volatiles were eliminated under reduced pressure at 45 °C giving a pale orange liquid, which solidified upon cooling. The crude product was dried under high vacuum (10.756 g, 92%). The crude product can be purified by sublimation at 90 °C under high vacuum to yield white crystals of **1** (8.972 g, 77%). DSC (T_{onset}, 5 °C min^{-1}): 147.4 °C (mp), >220 °C (dec); ^{1}H NMR (DMSO-d$_6$, 25 °C, ppm): δ = 7.58 (s (br), 1 H, N–H); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): δ = 111.6 (2 C, –CN), 123.7 (2 C, triazole); EA (C_4HN_5, 119.10): calcd C 40.34, H 0.85; N 58.81%; found: C 40.18, H 1.01 N 58.54%.

*General procedure for the synthesis of alkali metal salts of **1** (compounds **2–5**).* **1** (0.476 g, 4.0 mmol) was dissolved in ethanol (15 mL) and reacted with one equivalent of an alkali metal base, *i.e.*, 98% lithium hydroxide (0.098 g, 4.0 mmol), potassium hydroxide (0.224 g, 4.0 mmol), rubidium carbonate (0.462 g, 2.0 mmol) or cesium carbonate (0.652 g, 2.0 mmol). The reaction mixture was stirred for 1 h at room temperature (CO_2 evolution was observed for the synthesis of salts **4** and **5**), refluxed briefly and the solvent was removed under reduced pressure at 40 °C. The elemental analysis of compounds **2–5** showed the presence of two solvated water molecules for salt **2** whereas the remainder of the materials where obtained as anhydrous compounds.

Lithium 4,5-dicyano-1,2,3-triazolate dihydrate (2). White powder (0.602 g, 93% yield). DSC (T_{onset}, 5 °C min^{-1}): 322 °C (dec); MS (–c ESI): m/z = 117.9 (5, $[\mathrm{A}^-]^-$), 243.0 (100, $[2\mathrm{A}^- + \mathrm{Cat}^+]^-$), 368.3 (12, $[3\mathrm{A}^- + 2\mathrm{Cat}^+]^-$); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu}$ = 3408(w), 3377(w), 2252(s), 2147(m), 1504(m), 1421(w), 1368(m), 1280(w), 1247(m), 1188(m), 1165(m), 1154(m), 1008(w), 947(w), 861(w), 707(w), 651(m), 630(m), 525(w), 501(w), 492(w), 475(m), 447(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2246 (100), 1511 (16), 1390 (7), 1295 (12), 1155 (3), 1084 (8), 1001 (11), 717 (2), 658 (2), 524 (3), 469 (3); ^{1}H NMR (DMSO-d$_6$, 25 °C, ppm): δ = 3.58 ($\mathrm{H_2O}$); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): δ = 121.08 (2 C, –CN), 113.94 (2 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = +26 (1 N, s(br), $\nu_{1/2}$ = 690 Hz, N5), −24 (2 N, s(br), $\nu_{1/2}$ = 785 Hz, N4/N6), −122 (2 N, s(br), $\nu_{1/2}$ = 705 Hz, N1–N9); EA ($\mathrm{C_4H_4N_5O_2Li}$, 161.05): calcd C 29.83, H 2.50, N 43.49%; found: C 29.63, H 2.48, N 43.61%.

Potassium 4,5-dicyano-1,2,3-triazolate (3). White powder (0.761 g, 94% yield). DSC (T_{onset}, 5 °C min^{-1}): 314 °C (dec); MS (−c ESI): m/z = 118.0 (22, $[\mathrm{A}^-]^-$), 274.7 (38, $[2\mathrm{A}^- + \mathrm{Cat}^+]^-$), 431.6 (100, $[3\mathrm{A}^- + 2\mathrm{Cat}^+]^-$); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu}$ = 3428(w), 2248(s), 1528(w), 1503(w), 1421(w), 1377(m), 1283(w), 1243(w), 1189(m), 1170(m), 1159(m), 1110(w), 1086(w), 986(w), 863(w), 709(w), 657(w), 634(m), 527(m), 501(w), 476(m), 456(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2252 (100), 1504 (20), 1378 (12), 1284 (7), 1157 (2), 1083 (10), 999 (8), 711 (2), 656 (4), 529 (5), 473 (4); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): δ = 121.10 (2 C, –CN), 113.66 (2 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = +24 (1 N, s(br), $\nu_{1/2}$ = 700 Hz, N5), −22 (2 N, s(br), $\nu_{1/2}$ = 790 Hz, N4/N6), −121 (2 N, s(br), $\nu_{1/2}$ = 725 Hz, N1/N9); EA ($\mathrm{C_4N_5K}$ 157.17): calcd C 30.57, N 44.56%; found: C 30.48, N 44.37%.

Rubidium 4,5-dicyano-1,2,3-triazolate (4). White powder (0.778 g, 96% yield). Single crystals of **4** suitable for X-ray analysis were grown by slow evaporation of a solution of the compound in alcohol or hot water. DSC (T_{onset}, 5 °C min^{-1}): 297 °C (dec); MS (−c ESI): m/z = 118.0 (74, $[\mathrm{A}^-]^-$), 320.6 (100, $[2\mathrm{A}^- + \mathrm{Cat}^+]^-$), 479.5 (11); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu}$ = 3326(w), 2245(s), 2161(w), 1503(w), 1419(w), 1375(m), 1283(w), 1242(w), 1189(m), 1169(m), 1159(m), 1109(w), 1000(w), 943(w), 863(w), 708(w), 655(w), 634(m), 554(w), 528(m), 506(w), 493(w), 474(m), 459(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2248 (100), 1504 (24), 1376 (13), 1284 (6), 1160 (2), 1082 (11), 999 (5), 710 (3), 654 (7), 530 (8), 473 (6); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): δ = 120.96 (2 C, –CN), 113.84 (2 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = +22 (1 N, s(br), $\nu_{1/2}$ = 715 Hz, N5), −20 (2 N, s(br), $\nu_{1/2}$ = 750 Hz, N4–N6), −120 (2 N, s(br), $\nu_{1/2}$ = 690 Hz, N1–N9); EA ($\mathrm{C_4N_5Rb}$ 203.54): calcd C 23.60, N 34.41%; found: C 23.45, N 34.12%.

Cesium 4,5-dicyano-1,2,3-triazolate (5). White powder (0.972 g, 97% yield). DSC (T_{onset}, 5 °C min^{-1}): 294 °C (dec); MS (−c ESI): m/z = 118.0 (72, $[\mathrm{A}^-]^-$), 368.6 (100, $[2\mathrm{A}^- + \mathrm{Cat}^+]^-$); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu}$ = 3743(w), 3302(w), 2241(s), 2193(w), 1635(w), 1500(m), 1421(w), 1379(m), 1288(w), 1243(w), 1181(m), 1146(m), 1115(w), 1059(w), 1003(w), 946(w), 859(w), 733(w), 708(w), 635(m), 606(w), 588(w), 576(w), 567(w), 529(m), 515(w), 487(w), 479(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2250 (100), 1510 (19), 1381 (11), 1289 (8), 1157 (3), 1083 (9), 1001 (4), 712 (2), 655 (5), 525 (6), 468 (5); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): δ = 120.99 (2 C, –CN), 113.85 (2 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = +24 (1 N, s(br), $\nu_{1/2}$ = 645 Hz, N5), −18 (2 N, s(br), $\nu_{1/2}$ = 760 Hz, N4–N6), −122 (2 N, s(br), $\nu_{1/2}$ = 710 Hz, N1–N9); EA ($\mathrm{C_4N_5Cs}$ 250.98): calcd C 19.14, N 27.91%; found: C 18.89, N 27.68%.

*General procedure for the synthesis of alkaline earth metal salts of **1** (compounds **6–9**).* **1** (0.476 g, 4.0 mmol) was dissolved in distilled water (10 mL) and reacted with one equivalent of an alkali earth metal hydroxide, *i.e.*, 99% magnesium hydroxide (0.117 g, 2.0 mmol), 96% calcium hydroxide (0.154 g, 2.0 mmol), 95% strontium hydroxide (0.256 g, 2.0 mmol) or 98% barium hydroxide octahydrate (0.644 g, 2.0 mmol). An exothermic reaction was observed and the reaction mixture was stirred for 1 h at room temperature and briefly refluxed. The insoluble alkaline earth metal carbonate was filtered while hot and the solvent was eliminated under reduced pressure. Elemental analysis of the products showed the presence of eight solvated water molecules for compounds **6** and **7** and six solvated water molecules for compounds **8** and **9**.

Magnesium 4,5-dicyano-1,2,3-triazolate octahydrate (6). White powder (0.761 g, 94% yield). X-ray quality single crystals of **6** were grown by recrystallization from hot water. DSC (T_{onset}, 5 °C min^{-1}): 317 °C (dec); MS (−c ESI): m/z = 118.0 (100, $[\mathrm{A}^-]^-$), 236.5 (17, $[2\mathrm{A}]^-$), 378.8 (39, $[3\mathrm{A}^- + \mathrm{Cat}^{2+}]^-$), 413.1 (34); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu}$ = 3635(w), 3487(s), 3332(m), 3223(s), 2256(s), 2241(s), 1665(s), 1506(w), 1385(m), 1300(w), 1239(w), 1190(m), 1103(w), 996(w), 662(m), 639(m), 523(w), 506(w), 475(w), 462(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2258 (100), 2243 (71), 1507 (18), 1494 (14), 1387 (13), 1300 (11), 1191 (4), 1103 (17), 1019 (7), 710 (3), 658 (4), 525 (9), 471 (2); ^{1}H NMR (DMSO-d$_6$, 25 °C, ppm): δ = 3.83 ($\mathrm{H_2O}$); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): δ = 121.49 (4 C, –CN), 114.17 (4 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = +23 (1 N, s(br), $\nu_{1/2}$ = 700 Hz, N5), −22 (2 N, s(br), $\nu_{1/2}$ = 780 Hz, N4–N6), −121 (2 N, s(br),$\nu_{1/2}$ = 700 Hz, N1–N9); EA ($\mathrm{C_8H_{16}N_{10}O_8Mg}$ 404.58): calcd C 23.75, H 3.99, N 34.62%; found: C 23.53, H 4.12, N 34.48%.

Calcium 4,5-dicyano-1,2,3-triazolate octahydrate (7). White powder (0.802 g, 95% yield). DSC (T_{onset}, 5 °C min^{-1}): 308 °C (dec); MS (−c ESI): m/z = 118.0 (29, $[\mathrm{A}^-]^-$), 236.7 (32, $[2\mathrm{A}]^-$), 394.2 (100, $[3\mathrm{A}^- + \mathrm{Cat}^{2+}]^-$), 413.2 (29); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu}$ = 3574(w), 3467(w), 3394(m), 3231(s), 2252(m), 2242(m), 2114(w), 1653(s), 1599(s), 1548(w), 1462(w), 1416(m), 1368(w), 1302(w), 1277(w), 1192(w), 1179(m), 1141(w), 1115(w), 1093(w), 1061(w), 790(m), 698(m), 633(w), 577(m), 515(m), 483(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ =

2253 (100), 1609 (14), 1550 (26), 1416 (7), 1368 (8), 1302 (6), 1193 (7), 1179 (4), 1110 (15), 1099 (22), 1014 (12), 794 (3), 715 (11), 647 (3), 504 (4), 475 (4), 407 (6); ^{1}H NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = 3.60$ (H_2O); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = 121.21$ (4 C, –CN), 114.04 (4 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = +20$ (1 N, s(br), $\nu_{1/2} = 680$ Hz, N5), −20 (2 N, s(br), $\nu_{1/2} = 780$ Hz, N4/N6), −126 (2 N, s(br), $\nu_{1/2} = 710$ Hz, N1/N9); EA ($C_8H_{16}N_{10}O_8Ca$ 420.35): calcd C 22.86, H 3.84, N 33.32%; found: C 22.57, H 4.08, N 33.09%.

Strontium 4,5-dicyano-1,2,3-triazolate hexahydrate (8). White powder (0.798 g, 92% yield). Slow evaporation of a solution of **8** in hot water resulted in the formation of X-ray quality crystals of the tetrahydrate strontium salt of 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid (**8b**). DSC (T_{onset}, 5 °C min^{-1}): 334 °C (dec); MS (−c ESI): $m/z = 118.0$ (25, [A$^-$]$^-$), 236.7 (28, [2A]$^-$), 442.1 (100, [3A$^-$ + Cat^{2+}]$^-$), 495.9 (46); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu} = 3615$(w), 3462(w), 3240(m), 2246(m), 2163(w), 1662 (s), 1588(s), 1454(w), 1417(m), 1355(w), 1301(w), 1280(w), 1203(m), 1185(m), 1150(w), 1112(w), 1039(w), 790(w), 698 (m), 644(m), 545(w), 508(w), 482(m), 459(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 2247$ (100), 1668 (4), 1592 (14), 1541 (21), 1418 (5), 1359 (2), 1301 (2), 1184 (5), 1113 (11), 1016 (9), 791 (2), 701 (9), 650 (2), 496 (2), 429 (2); ^{1}H NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = 3.52$ (H_2O); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = 121.17$ (4 C, –CN), 114.02 (4 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = +22$ (1 N, s (br), $\nu_{1/2} = 665$ Hz, N5), −20 (2 N, s(br), $\nu_{1/2} = 815$ Hz, N4/N6), −124 (2 N, s(br), $\nu_{1/2} = 700$ Hz, N1/N9); EA ($C_8H_{12}N_{10}O_6Sr$ 431.86): calcd C 22.24, H 2.80, N 32.43%; found: C 21.93, H 3.02, N 32.14%.

Barium 4,5-dicyano-1,2,3-triazolate hexahydrate (9). White powder (0.924 g, 96% yield). DSC (T_{onset}, 5 °C min^{-1}): 351 °C (dec); MS (−c ESI): $m/z = 118.0$ (39, [A$^-$]$^-$), 236.7 (38, [2A]$^-$), 492.0 (100, [3A$^-$ + Cat^{2+}]$^-$), 546.0 (17); IR (golden gate, cm^{-1}, rel. int.): $\tilde{\nu} = 3454$(m), 3322(w), 3128(m), 2240(m), 2114(w), 1657(s), 1577(m), 1523(s), 1434(s), 1356(m), 1289(w), 1175 (m), 1151(m), 1086(w), 1011(w), 798(m), 781(w), 739(w), 718 (m), 633(w), 558(m), 502(w), 483(w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 2244$ (100), 1675 (3), 1583 (15), 1527 (27), 1437 (11), 1359 (5), 1291 (8), 1178 (10), 1112 (13), 1087 (5), 1012 (9), 786 (1), 723 (7), 495 (3), 427 (5); ^{1}H NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = 3.43$ (H_2O); ^{13}C NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = 121.06$ (4 C, –CN), 113.93 (4 C, triazole); ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): $\delta = +25$ (1 N, s(br), $\nu_{1/2} = 680$ Hz, N5), −26 (2 N, s(br), $\nu_{1/2} = 790$ Hz, N4–N6), −120 (2 N, s (br), $\nu_{1/2} = 700$ Hz, N1–N9); EA ($C_8H_{12}N_{10}O_6Ba$ 481.57): calcd C 19.95, H 2.51, N 29.08%; found: C 19.77, H 2.73, N 28.87%.

Conclusion

We considered 4,5-dicyano-2*H*-1,2,3-triazole (**1**) for the synthesis of energetic salts with alkali (**2–5**) and alkaline earth (**6–9**) metals. All materials were readily synthesized from cheap starting materials in excellent yields and high purities and characterized by analytical (mass spectrometry and elemental analysis) and spectroscopic (infrared, Raman and multinuclear NMR) methods. Additionally, we solved the solid state structure of the 4,5-dicyano-2*H*-1,2,3-triazole anion of one of the alkali (**4**) and one of the alkaline earth (**6**) metal salts. Except for the lithium salt (**2**), which is hygroscopic, the remainder of the compounds are stable to moisture, do not show any sign of decomposition upon storage and have good solubility properties. Interestingly, the strontium salt **8** hydrolyses in hot water to form the previously unknown 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid salt (compound **8b**), as supported by X-ray measurements. For both the 4,5-dicyano-2*H*-1,2,3-triazole and the 5-cyano-2*H*-1,2,3-triazole-4-carboxylic acid anions we computed the NBO and Mülliken charges. Lastly, we assessed the thermal stabilities of compounds **2–9** by means of differential scanning calorimetry and the sensitivities towards classical stimuli were measured using standard BAM tests. Compounds **2–9** combine good burning behaviours with excellent thermal stabilities and low sensitivities, making the materials of prospective interest for energetic applications.

Acknowledgements

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