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Synthesis and structural characterization of 3,5-dinitro-1,2,4-triazolates

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Salts of 3,5-dinitro-1*H*-1,2,4-triazole, a building block for energetic materials, have been prepared and fully characterized. Most of the studied salts exhibit high thermal stability and very low shock and friction sensitivities. 3,5-dinitro-1,2,4-triazolates with the nitrogen-rich ammonium, guanidinium, aminoguanidinium, and aminotetrazolium cations are energetic and have potential for energetic material applications. Salts containing alkali, alkali earth metal, and silver cations exhibit coloured emissions upon combustion while salts with large organic cations such as PPh_4^+ and $(Ph_3P)_2N^+$ are highly insensitive and can be easily crystallized.

Introduction

In recent years, the development of new, environmentally friendly energetic materials has sparked considerable attention in the synthetic community.[1] Nitrogen-rich cyclic compounds, such as triazoles and tetrazoles, are important and versatile motifs for energetic materials. These heterocycles can be further functionalized with explosophore groups, such as nitro, *N*-nitro, azo, or azido. Among these, 3-nitro-1*H*-1,2,4-triazole[2-5] and 3,5-dinitro-1*H*-1,2,4-triazole (HDNT)[6, 7] have attracted considerable interest for energetic material and high oxygen carrier applications. With five nitrogen and four oxygen atoms per molecule, the latter combines the advantages of a high nitrogen and high oxygen content in a single compound. Since the first preparation of HDNT,[8, 9] a significant number of derivatives have been reported,[5, 10-14] including complex borate anions.[15] During the course of our on-going research on environmental-benign energetic materials and high-oxygen,[15-18] we obtained characterization data and crystal structures for several 3,5-dinitro-1,2,4-triazolates that we wish to share with the broader scientific community. Although several simple salts containing the 3,5-dinitro-1,2,4-triazolate (DNT) anion have been described in the literature,[19-29] they have not been fully characterized. In this work nineteen different salts of the DNT anions have been prepared and fully characterized, including their crystal structures, thermal stability, and friction and impact sensitivities.

Experimental Part

Caution! The compounds of this work are energetic materials that might explode under certain conditions (e.g., elevated temperature, impact, friction or electric discharge). Appropriate safety precautions,[30] such as the use of shields or barricades in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves and suits made from leather and/or Kevlar) should be taken all the time when handling these materials. **Ignoring safety precautions may lead to serious injuries!**

Materials and apparatus

All chemicals and solvents were obtained from Sigma-Aldrich or Alfa-Aesar and were used as supplied. NMR spectra were recorded at 298 K on Bruker AMX500 or Varian VNMRS-600s spectrometers using $(CD_3)_2CO$ or D_2O solutions in standard 5 mm o.d. glass tubes. Chemical shifts are given relative to neat tetramethylsilane (^1H, ^{13}C) or neat CH_3NO_2 (^{14}N, ^{15}N). Raman spectra were recorded at ambient temperatures in Pyrex glass tubes in the range of 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm or a Cary 83 spectrometer using an Ar laser at 488 nm. Infrared spectra were recorded in the range 4000-400 cm^{-1} on Midac, M Series spectrometer using KBr pellets or on a Bruker Optics Alpha FT-IR ATR spectrometer. KBr pellets were prepared very carefully using an Econo mini-press (Barnes Engineering Co.). Differential thermal analysis (DTA) curves were recorded with a purge of dry nitrogen gas and a heating rate of 5 °C/min on an OZM Research DTA552-Ex instrument with the Meavy 2.2.0 software. The sample sizes were 3-15 mg. The impact and friction sensitivity data were determined on an OZM Research BAM Fall Hammer BFH-10 and an OZM Research BAM Friction apparatus FSKM-10, respectively, through five individual measurements that were averaged. Both instruments were calibrated using RDX.

The 3,5-dinitro-1*H*-1,2,4-triazole was prepared according to a modified literature method by diazotation of 3,5-diamino-3*H*-1,2,4-triazole.[31]

General procedure for the synthesis of DNT salts from carbonates

A solution of HDNT (235 mg, 1.5 mmol) in 5 mL acetone was added to a stirred suspension of the corresponding carbonate (8-15 mmol) in 30 mL acetone. After stirring for several hours, the suspension was filtered and the solid residue was washed with acetone. The resulting pale yellow filtrate was taken to dryness by evaporation in air.

General procedure for the synthesis of DNT salts by precipitation

A solution of HDNT (235 mg, 1.5 mmol) in 5 mL of water was added to an aqueous solution of $AgNO_3$, PPh_4Cl or PPNCl. The white precipitate was filtered off and washed with water.

General procedure for the synthesis of DNT salts by neutralization; method 1

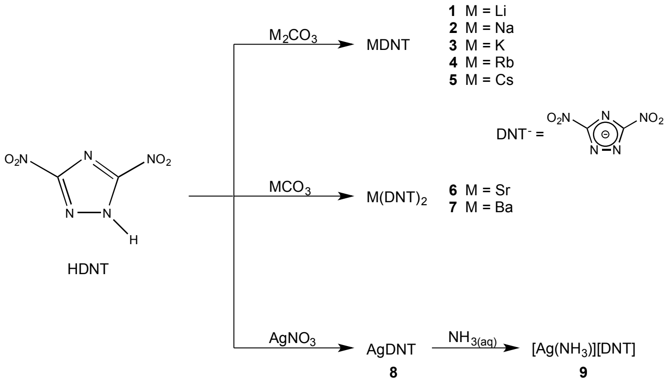
A solution of HDNT (235 mg, 1.5 mmol) in 5 mL ethanol was added to an excess of aqueous ammonia, diethylamine, triethylamine or pyridine. The obtained pale yellow solution was taken to dryness by evaporation in air.

General procedure for the synthesis of DNT salts by neutralization; method 2

A solution of HDNT (235 mg, 1.5 mmol) in 5 mL ethanol was added to a stoichiometric amount of 5-aminotetrazole or tetramethylammonium hydroxide in ethanol. The obtained pale yellow solution was taken to dryness by evaporation in air.

X-ray crystal structure determination

The single crystal X-ray diffraction data of compounds **3**$\cdot H_2O$, **4**, **5**, and **9** were collected on a Bruker SMART diffractometer equipped with an APEX CCD detector, using Mo K_α radiation (graphite monochromator) from a fine-focus tube. The single crystal X-ray diffraction data of the remaining compounds were collected on a Bruker SMART APEX DUO diffractometer, equipped with an APEX II CCD detector, using Mo K_α radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube or Cu K_α radiation (multi-layer optics) from an IμS microsource. The frames were integrated using the SAINT algorithm[32] to give the hkl files corrected for Lp/decay. The absorption correction was performed using the SADABS program.[33] The structures were solved and refined on F^2 using the Bruker SHELXTL software package.[34, 35] All non-hydrogen atoms were refined anisotropically. Unless noted otherwise, the positions of hydrogen atoms have been located from the difference electron density map. ORTEP drawings were prepared using the ORTEP-III for Windows V2.02 program.[36] Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1006182 (**11**), 1006181 (**12a**) 1013941 (**12b**), 1006639 (**13**), 1014382 (**14**), 1006408 (**15**), 1009537 (**17**), 1006184 (**18**), 1031353 (**19**) and from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD 427905 (**1**$\cdot 2H_2O$), 427851 (**2**$\cdot 2H_2O$), 427971 (**3**), 427853 (**3**$\cdot 2H_2O$), 427852 (**4**), 427854 (**5**), 428080 (**6**$\cdot 6H_2O$), 428122 (**7**$\cdot 11H_2O$), 427855 (**9**), 428079 (**10**$\cdot 2H_2O$), 427856 (**16**$\cdot H_2O$).

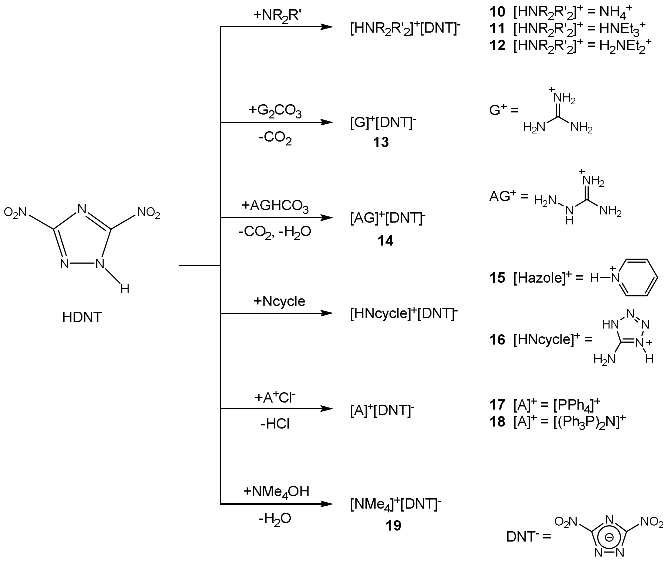


Scheme 1: Synthesis of the DNT metal salts **1**-**9**.

Results and discussion

Synthesis

For the synthesis of LiDNT (**1**), NaDNT (**2**), KDNT (**3**), RbDNT (**4**), CsDNT (**5**), $Sr(DNT)_2$ (**6**), and $Ba(DNT)_2$ (**7**), the parent triazole HDNT was dissolved in acetone that contained a few drops of water and stirred over a suspension containing an excess of the corresponding metal carbonate (Scheme 1).[8]



Scheme 2: Synthesis of DNT salts **10**-**19**

With the exception of barium and strontium carbonate that remained white, the insoluble carbonate turned orange to reddish brown and the solution became light yellow. The reaction mixtures were filtered and crystals were grown from the filtrates by slow evaporation of the solvent. The alkali and alkali earth metal salts were obtained as light yellow to orange crystalline solids. Crystals of the water-free potassium salt **3** were obtained by recrystallization of the reaction product from acetone solution. The compound is hygroscopic and forms the dihydrate upon prolonged exposure to air. The DNT silver salt **8**[8, 31] was obtained as a white amorphous precipitate when a silver nitrate solution was added to an aqueous solution of HDNT. Orange single crystals of $Ag(NH_3)DNT$ **9** were obtained when compound **8** was dissolved in aqueous ammonia and the solvent was allowed to evaporated. The ammonium salt NH_4DNT[25] was prepared by reacting HDNT with NH_3 (Scheme 2). Yellow crystals of the dihydrate $NH_4DNT{\cdot}2H_2O$ were obtained by slow evaporation of an aqueous solution of **10**.

For the synthesis of the triethylammonium salt **11**, diethylammonium salt **12** and pyridinium salt **15**, an excess of the corresponding amine was added to an aqueous solution of HDNT. Yellow to orange crystals were obtained by slow evaporation of the solvent. Guanidinium 3,5-dinitro-1,2,4-triazolate **13**[8] was obtained by stirring an acetone solution of HDNT over guanidine carbonate followed by filtration and slow evaporation of the solvent, yielding a crystalline orange material (Scheme 2). Similarly, aminoguanidium DNT **14** was obtained as a yellow-orange crystalline solid from aminoguanidine bicarbonate and HDNT in ethanol. Colorless aminotetrazolium 3,5-dinitro-1,2,4-triazolate **16**[7] was obtained from stoichiometric amounts of 5-aminotetrazole and HDNT in aqueous solution.

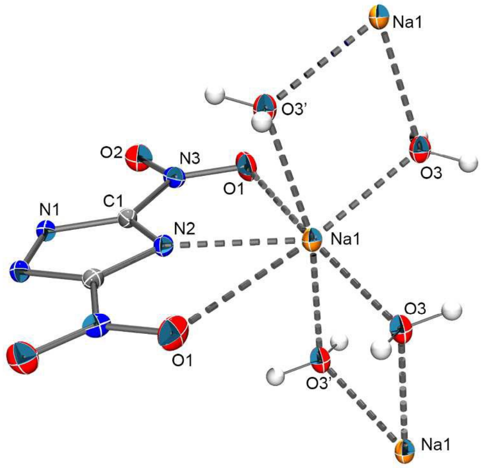


Figure 1: The solid-state structure of $NaDNT{\cdot}2H_2O$ **2**$\cdot 2H_2O$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond distances (Å): Na1-N2 2.380(1), Na1-O1 3.033(1), Na1-O3 2.340(1), Na1-O3' 2.469(1).

The tetraphenylphosphonium (PPh_4)[27] and bis(triphenylphosphoranylidene)ammonium (PPN) salts **17** and **18**, respectively, were precipitated from an aqueous solution of HDNT by addition of aqueous solutions of PPh_4Cl and PPNCl, respectively. The colorless to off-white precipitates were thoroughly washed with water. Crystalline compounds were obtained by recrystallization from acetone. The properties of PPh_4DNT are in good agreement with those previously reported.[27] The tetramethylammonium (TMA) salt **19**[23] was obtained from stoichiometric amounts of tetramethylammonium hydroxide and HDNT in aqueous solution. Single crystals were grown by recrystallization of the crude product from ethanol solution. The obtained materials were characterized by multi-nuclear NMR and vibrational spectroscopy, as well as their X-ray crystal structure.

X-ray Crystal Structures

Single crystals suitable for X-ray crystal structure determination were obtained for the metal salts $LiDNT{\cdot}2H_2O$ **1**$\cdot 2H_2O$, $NaDNT{\cdot}2H_2O$ **2**$\cdot 2H_2O$, KDNT **3**, $KDNT{\cdot}2H_2O$ **3**$\cdot 2H_2O$, RbDNT **4**, CsDNT **5**, $Sr(DNT)_2{\cdot}6H_2O$ **6**$\cdot 6H_2O$, $Ba(DNT)_2{\cdot}11H_2O$ **7**$\cdot 11H_2O$, and $Ag(NH_3)DNT$ **9**. Structures were also obtained for the ammonium salts $NH_4DNT{\cdot}2H_2O$ **10**$\cdot 2H_2O$, $[HNEt_3][DNT]$ **11**, $[H_2NEt_2][DNT]$ **12**, the guanidinium salt **13**, the aminoguanidinium salt **14**, monohydrates of the pyridinium salt **15**$\cdot H_2O$ and aminotetrazolium salt **16**$\cdot H_2O$, as well as $[PPh_4][DNT]$ **17**, [PPN][DNT] **18**, and $[NMe_4][DNT]$ **19**.

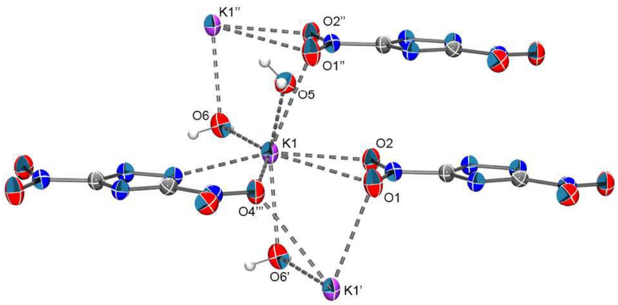
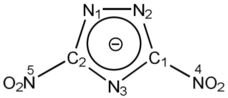


Figure 2: The solid-state structure of the potassium salt **3**$\cdot 2H_2O$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond distances (Å): K1-O1 3.144(3), K1-O1'' 3.143 (3), K1-O2 2.906(3), K1-O4''' 2.909(3), K1-O5 2.770(3), K1-O6 2.703(3), K1-O6' 2.832(3).

The geometry of the five-membered ring in the dinitrotriazole anion remains virtually unchanged throughout the investigated structures. The N-N bond distances range from 1.350(2) to 1.368(5) Å, the C-N distances from 1.315(2) to 1.347(7) Å and the C-NN distances from 1.316(6) to 1.351(8) Å. Selected bond lengths and bond angles of the 3,5-dinitro-1,2,4-triazolate anion in the different alkali metal salts are summarized in Table 1. In the investigated salts, the DNT anion usually adopts a geometry in which both NO_2 groups are almost coplanar with the plane of the five-membered triazole ring. The torsion angles for the NO_2 groups with respect to the triazole ring plane were found to be less than 6° for most salts. The major exception is the rubidium salt **4** for which torsion angles of 4.6° and 19.1° were found.

The relevant data and parameters for the X-ray measurements and structure refinements of the 3,5-dinitro-1,2,4-triazolates are summarized in Tables 2-4. Further crystallographic data and representations of the unit cells for all crystal structures can be found in the Electronic Supplementary Information.

Table 1: Selected bond lengths [Å] and angles [°] for the alkali metal salts **1**-**5**.

						
	LiDNT·2H_2O **1**·2H_2O	NaDNT·2H_2O **2**·2H_2O	KDNT **3**^{a}	KDNT·2H_2O **3**·2H_2O	RbDNT **4**	CsDNT **5**
N1-N2	1.366(1)	1.366(1)	1.368(5)	1.359(4)	1.353(7)	1.364(4)
C1-N2	1.336(1)	1.336(1)	1.331(5)	1.322(4)	1.338(7)	1.339(4)
C1-N3	1.336(1)	1.331(1)	1.322(5)	1.329(4)	1.343(7)	1.326(4)
C1-N4	1.449(1)	1.451(1)	1.445(5)	1.445(5)	1.431(7)	1.445(5)
C2-N1	1.336(1)	1.336(1)	1.327(6)	1.336(4)	1.341(7)	1.336(5)
C2-N3	1.336(1)	1.331(1)	1.325(5)	1.333(5)	1.319(7)	1.331(5)
C2-N5	1.449(1)	1.451(1)	1.448(6)	1.446(4)	1.433(7)	1.440(4)
N1-N2-C1	104.12(5)	104.07(4)	103.2(3)	104.3(3)	104.3(5)	103.7(3)
N2-C1-N3	116.84(8)	116.73(7)	117.6(4)	117.2(3)	116.4(5)	117.1(3)
C1-N3-C2	98.09(10)	98.39(9)	97.9(3)	98.1(3)	98.0(4)	97.9(3)
N3-C2-N1	116.84(8)	116.73(7)	117.1(4)	116.3(3)	117.2(5)	117.3(3)
C2-N1-N2	104.12(5)	104.07(4)	104.1(3)	104.2(3)	104.1(5)	104.0(3)

^{a} Values given for one of the two independent anions of the asymmetric unit.

Table 2: Crystallographic data for the DNT metal salts.

	1·2H_2O	**2**·2H_2O	**3**	**3**·2H_2O	**4**	**5**	**6**·6H_2O	**7**·11H_2O	**9**
formula	$C_2H_4LiN_5O_6$	$C_2H_4N_5NaO_6$	$C_2KN_5O_4$	$C_2H_4KN_5O_6$	$C_2N_5O_4Rb$	$C_2CsN_5O_4$	$C_4H_{12}N_{10}O_{14}Sr$	$C_4H_{22}BaN_{10}O_{19}$	$C_2H_3AgN_6O_4$
mol wt [g/mol]	201.04	217.09	197.17	233.20	243.54	290.98	511.86	651.65	282.97
temp [K]	100(2)	100(2)	100(2)	130(2)	140(2)	133(2)	100(2)	100(2)	140(2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/n$	$P1$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P2_1/m$	$P2_1/n$
a [Å]	15.342(2)	15.3444(7)	6.741(2)	4.5220(15)	7.6561(12)	7.974(3)	9.2895(3)	6.9239(6)	7.8061(19)
b [Å]	8.3048(11)	8.7270(4)	12.997(4)	6.355(2)	7.8172(12)	10.088(3)	12.8551(4)	18.7743(15)	5.5756(14)
c [Å]	6.3573(8)	6.6379(3)	14.749(5)	7.770(3)	11.0946(17)	9.267(3)	16.5552(7)	9.2088(7)	17.034(4)
α [deg]	90	90	90	96.093(4)	90	90	108.2150(10)	90	90
β [deg]	113.079(2)	114.9340(6)	97.697(5)	92.533(4)	90	109.941(4)	90.8870(10)	111.6350(10)	101.686(3)
γ [deg]	90	90	90	108.569(4)	90	90	111	90	90
V [$Å^3$]	745.17(17)	806.04(6)	1280.6(7)	209.75(12)	664.00(18)	700.8(4)	1736.03(11)	1112.73(16)	726.0(3)
Z	4	4	8	1	4	4	4	2	4
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calc} [g/cm^3]	1.792	1.789	2.045	1.846	2.436	2.758	1.958	1.945	2.589
μ [mm^{-1}]	0.172	0.216	0.813	0.652	7.440	5.269	3.204	1.891	2.773
F(000)	408	440	784	118	464	536	1024	648	544
reflns collected	8446	9609	14946	2303	4210	3944	42154	26945	4279
ind reflns	1124	1231	3713	1445	1583	1589	10328	3476	1688
R_{int}	0.0269	0.0207	0.0395	0.0228	0.0400	0.1014	0.0331	0.0424	0.0176
no. of parameters	71	72	217	127	109	109	619	178	130
R_1 [$I > 2\sigma(I)$]	0.0311	0.0237	0.0764	0.0255	0.0335	0.0332	0.0240	0.0370	0.0185
wR_2 [$I > 2\sigma(I)$]	0.0850	0.0662	0.1578	0.0714	0.0703	0.0848	0.0491	0.0831	0.0476
GOF	1.077	1.095	1.277	1.138	0.998	1.040	1.032	1.204	1.084

The relevant data and parameters for the X-ray measurements and structure refinements of the 3,5-dinitro-1,2,4-triazolates are summarized in Tables 2-4. Further crystallographic data and representations of the unit cells for all crystal structures can be found in the Electronic Supplementary Information.

Crystallized from acetone solutions and exposed to ambient air, the lithium, sodium and potassium DNT salt crystals contain two molecules of water per formula unit, whereas the rubidium and cesium salts crystallize free of water.

We also obtained water-free single crystals of the potassium salt of DNT. Selected crystallographic data for the alkali metal and ammonium salts are compiled in Table 2.

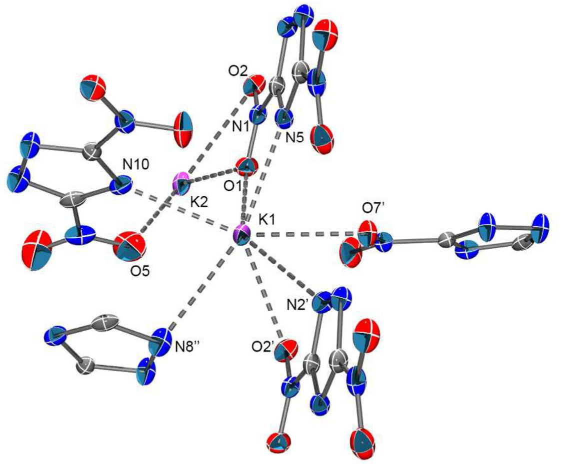


Figure 3: The solid-state structure of KDNT **3**. Thermal ellipsoids are shown at the 50% probability level. Some nitro groups have been omitted for clarity. Selected bond distances (Å): K1-N2' 2.871(4), K1-N5 2.714(4), K1-N8'' 3.017(4), K1-N10 2.829(4), K1-O1 2.967(4), K1-O2' 2.775(3), K1-O7' 2.826(4), K2-O1 2.866(4), K2-O2 3.191(3), K2-05 3.146(5).

The alkali metal salts LiDNT **1** and NaDNT **2** crystallize as dihydrates in the monoclinic space group *C*2/*c* with four formula units in the unit cell (Z = 4). The solid-state structures of MDNT·$2H_2O$ (M = Li **1**·$2H_2O$, Na **2**·$2H_2O$) do not consist of isolated ions but are dominated by interactions between the metal cation and a nitrogen atom of the triazole ring as well as two oxygen atoms from individual nitro groups of the anion. The structures of the lithium and sodium salts are quite similar. The solid-state structure of **2**·$2H_2O$ is depicted in Figure 1. The structure of the lithium salt is shown in the Supplementary Information. In addition, each metal ion is surrounded and coordinated by four water molecules that act as bridging ligands to two neighbouring metal ions. Selected bond lengths and angles are listed in Table 1.

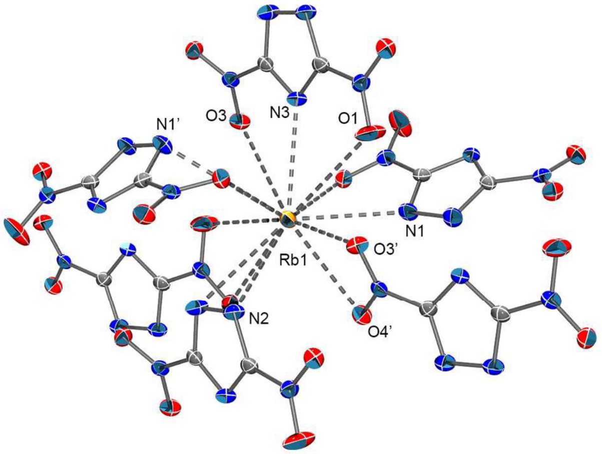


Figure 4: The solid-state structure of the rubidium salt **4**. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Rb1-N1 3.340(5), Rb1-N2 3.421(5), Rb1-N3 3.019(4), Rb1-O1 3.379(5), Rb1-O3 3.676(4), Rb1-O3' 3.076(4), Rb1-O4' 3.197(4).

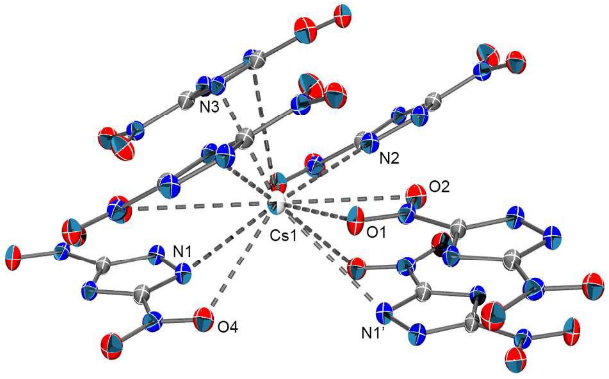


Figure 5: The solid-state structure of the caesium salt **5**. Thermal ellipsoids are shown at the 50% probability. Selected bond distances (Å): Cs1-N1 3.340(3), Cs-N1' 3.591(4), Cs1-N2 3.236(3), Cs1-N3 3.207(4), Cs1-O1- 3.288(3), Cs1-O2 3.392(3), Cs1-O4 3.233(3).

The dihydrate of the potassium salt **3**·$2H_2O$ crystallizes in space group *P*1, with one formula unit per unit cell (*Z* = 1). The solid-state structure is dominated by cation-anion interactions (Figure 2). Four oxygen atoms and a nitrogen atom from three anions as well as three water molecules coordinate the potassium cations. Two of the water molecules are bridging two individual cations, while the third water molecule is terminal. Selected bond lengths and angles are listed in Table 1.

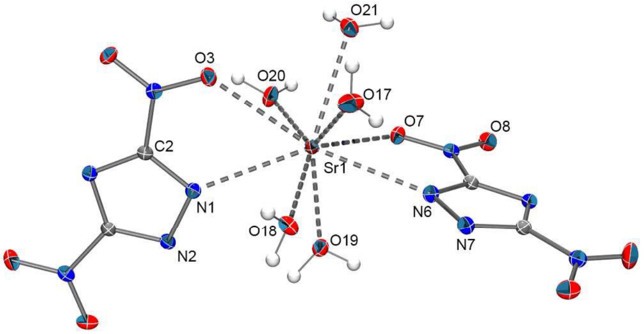


Figure 6: One of the two independent $Sr(H_2O)_5(DNT)_2$ units in the solid-state structure of $Sr(DNT)_2$·6 H_2O **6**·$6H_2O$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond distances (Å): Sr1-N1 2.773(2), Sr1-N6 2.741(1), Sr1-O3 2.720(1), Sr1-O7 2.798(1), Sr1-O17 2.578(1), Sr1-O18 2.601(1), Sr1-O19 2.548(1), Sr1-O20 2.618(1), Sr1-O21 2.709(2).

The water-free potassium salt **3** crystallizes in the monoclinic space group $P2_1$/n with eight molecules units per unit cell (*Z* = 8). The asymmetric unit of the crystal structure consists of two KDNT units. Selected bond lengths and angles are listed in Table 1. The solid-state structure is dominated by interactions between the metal cations and the nitrogen and oxygen atoms of the DNT anions (Figure 3). The closest K-N and K-O distances are 2.714(3) and 2.888(4) Å, respectively.

The rubidium salt **4** and the caesium salt **5** of DNT crystallize in space group $P2_12_12_1$ and $P2_1/n$, respectively, with four formula units per unit cell. Both solid-state structures do not consist of isolated ions but show interactions between the metal cations and the nitrogen atoms of the triazole ring as well as oxygen atoms of the nitro groups (Figures 4 and 5). The closest Rb-N and Cs-N distances are 3.019(4) and 3.207(4) Å, respectively, and the closest Rb-O and Cs-O are 3.004(4) and 3.212(3) Å, respectively.

The strontium salt $Sr(DNT)_2$ **6** crystallizes in the triclinic space group $P\overline{1}$ with six molecules of water per Sr atom. The structure consists of two symmetry independent $Sr(H_2O)_5(DNT)_2$ units in which the Sr atom is coordinated by five water molecules and by two nitrogen and two oxygen atoms from the two DNT anions (Figure 6). The last water molecule is not coordinated to the metal atom so that the structure can be described as $Sr(H_2O)_5(DNT)_2 \cdot H_2O$.

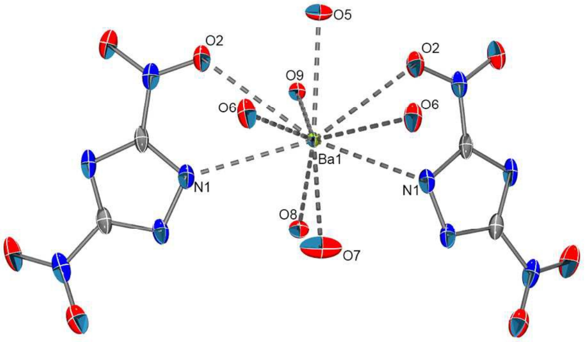


Figure 7: A $Ba(H_2O)_6(DNT)_2$ unit in the solid-state structure of $Ba(H_2O)_6(DNT)_2 \cdot 11\ H_2O$ **7**$\cdot 11H_2O$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted due to difficulties in determining their positions. Selected bond distances (Å): Ba1-N1 2.987(5), Ba1-O2 3.143(5), Ba1-O5 2.865(5), Ba1-O6 2.854(5), Ba1-O7 2.680(5), Ba1-O8 2.754(5), Ba1-O9 2.761(5).

The barium salt $Ba(DNT)_2$ **7** crystallizes in the monoclinic space group $P2_1/m$ with a total of eleven molecules of water per metal atom. The solid-state structure consists of two symmetry-related units. Each unit consists of a central barium atom that is coordinated by two nitrogen and two oxygen atoms from two DNT anions. Due to the larger ionic radius compared to strontium, the barium atom is also coordinated by six water molecules instead of only five for the strontium salt (Figure 7). The remaining five water molecule are not coordinated to the metal atom so that the structure can be described as $Ba(H_2O)_6(DNT)_2 \cdot 5\ H_2O$. Selected crystallographic data for **6**$\cdot 6H_2O$ and **7**$\cdot 11H_2O$ are compiled in Table 2. Unfortunately, the quality of the obtained single crystals of the Ba compound was rather poor and it was not possible to determine the positions of all hydrogen atoms in the structure.

All attempts to grow single crystals of AgDNT **8** suitable for X-ray structure determination were unsuccessful. Recrystallization of an amorphous sample of **8** from an aqueous ammonia solution resulted in crystals of the ammonia adduct $Ag(NH_3)DNT$ **9** instead.

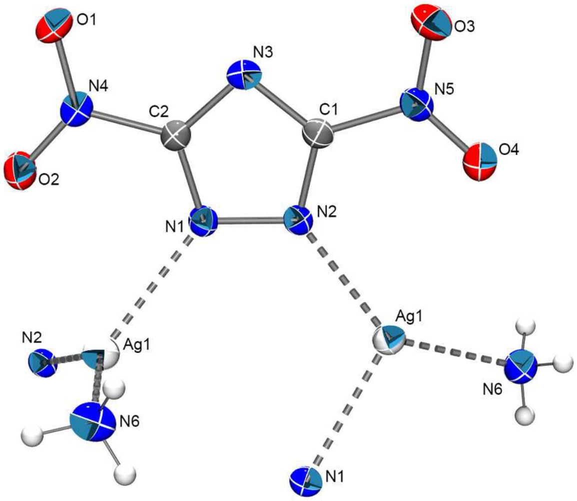


Figure 8: The solid-state structure of $Ag(NH_3)DNT$ **9**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond distances (Å): Ag1-N1 2.393(2), Ag1-N2 2.242(2), Ag1-N6 2.198(2).

The silver ammonia compound **9** crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell (Z = 4). Selected crystallographic data of $Ag(NH_3)DNT$ are listed in Table 2.

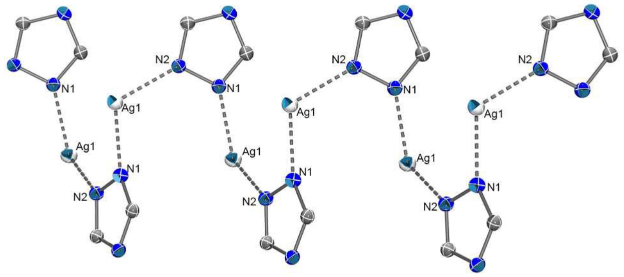


Figure 9: Part of a helical chain in the solid-state structure of $Ag(NH_3)DNT$ **9**. The nitro groups and ammonia ligands have been omitted for clarity.

The solid-state structure of **9** contains silver atoms coordinated by one NH_3 molecule that are linked in a 1,2-fashion to bridging DNT anions (Figure 8). The resulting helical chains of AgDNT units are oriented parallel along the *b*-axis of the crystal. Part of a helical chain is depicted in Figure 9.

Table 3: Crystallographic data for the DNT salts **10-16**.

	10·2H$_2$O	**11**	**12a**	**12b**	**13**	**14**	**15**·H$_2$O	**16**·H$_2$O
formula	$C_2H_8N_6O_6$	$C_8H_{16}N_6O_4$	$C_6H_{12}N_6O_4$	$C_6H_{12}N_6O_4$	$C_3H_6N_8O_4$	$C_3H_7N_9O_4$	$C_7H_8N_6O_5$	$C_3H_6N_{10}O_5$
mol wt [g/mol]	212.14	260.27	232.22	232.20	218.16	233.18	256.19	262.18
temp [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/c$	$C2/c$	$P2_12_12_1$
a [Å]	4.653(3)	7.0842(5)	6.4659(4)	7.3101(9)	8.3235(7)	9.0616(3)	13.9051(6)	6.0692(3)
b [Å]	6.461(4)	9.3195(6)	8.9964(6)	8.1876(10)	16.7996(14)	16.2452(5)	26.2532(12)	17.6181(8)
c [Å]	7.619(4)	19.3391(13)	18.8357(12)	9.9470(12)	12.3068(10)	6.5935(2)	6.3689(3)	19.4400(9)
α [deg]	93.105(7)	90	90	73.347(3)	90	90	90	90
β [deg]	93.948(7)	100.3110(11)	99.5420(10)	73.673(2)	102.3250(13)	110.189(3)	111.9480(7)	90
γ [deg]	108.360(7)	90	90	77.130(3)	90	90	90	90
V [Å^3]	216.2(2)	1256.17(15)	1080.51(12)	540.79(11)	1681.2(2)	910.98(5)	2156.48(17)	2078.68(17)
Z	1	4	4	2	8	4	8	8
λ [Å]	0.71073	0.71073	0.71073	1.54178	0.71073	1.54178	0.71073	0.71073
ρ_{calc} [g/cm^3]	1.630	1.376	1.427	1.426	1.724	1.700	1.578	1.676
μ [mm^{-1}]	0.158	0.111	0.120	1.036	0.155	1.338	0.136	0.153
F(000)	110	552	488	244	896	480	1056	1072
reflns collected	2547	29946	24237	8580	20271	12104	26448	35316
ind reflns	1599	3841	2903	1606	2562	1692	3279	6290
R_{int}	0.0122	0.0325	0.0293	0.0255	0.0333	0.0474	0.0274	0.0344
no. of parameters	159	169	153	153	160	201	174	373
R_1 [I > 2σ(I)]	0.0264	0.0397	0.0318	0.0267	0.0420	0.0790	0.0345	0.0372
wR_2 [I > 2σ(I)]	0.0610	0.0959	0.0842	0.0671	0.1147	0.2765	0.0974	0.0797
GOF	1.075	1.042	1.034	1.029	1.075	1.220	1.064	1.060

The dihydrate of the ammonium salt NH_4DNT **10** crystallizes in the triclinic space group $P1$ with one formula unit per unit cell (Figure 10).

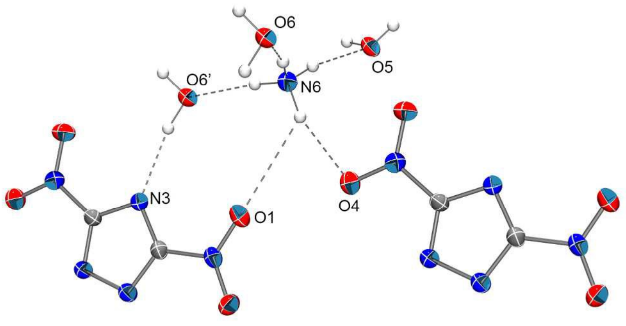


Figure 10: Hydrogen bonding in the solid-state structure of $NH_4DNT{\cdot}2H_2O$ **10**·2H$_2$O. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected distances (Å): N3-O6' 2.852(3), N6-O1 3.453(3), N6-O4 3.050(3), N6-O5 2.862(3), N6-O6 2.885(3), N6-O6' 2.828(4).

The solid-state structure consists of ammonium cations and DNT anions that are associated through hydrogen bonds. Hydrogen bonding is observed with water molecules as donor and DNT$^-$ as acceptor sites and also between water molecules and the NH_4^+ cation as acceptor. Selected crystallographic data for **10**·H$_2$O are listed in Table 3.

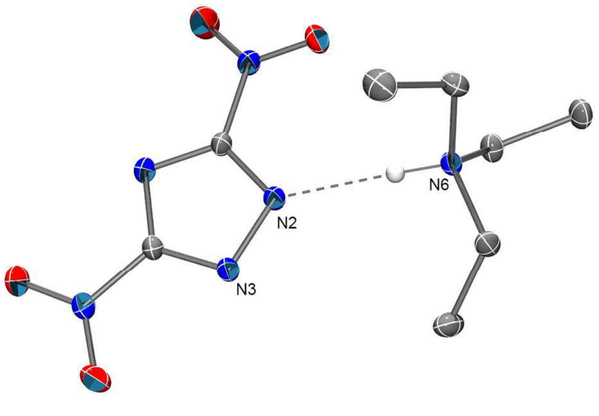


Figure 11: Hydrogen bonding in the triethylammonium salt **11**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms of the alkyl chains have been omitted for clarity. Depicted hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. The N2-N6 distance is 2.947(1) Å.

The triethylammonium salt of 3,5-dinitro-1H-1,2,4-triazole **11** crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell. As expected, the solid-state structure is dominated by hydrogen bonding between the cation and the anion (Figure 11). The crystallographic parameters of the structure are summarized in Table 3.

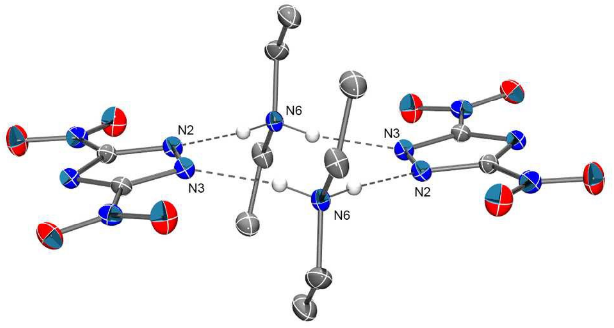


Figure 12: Hydrogen bonding in the diethylammonium salts **12a** and **12b**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms of the alkyl chains have been omitted for clarity. Depicted hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected atomic distances in the monoclinic [triclinic] polymorph (Å): N2-N6 2.929(1) [2.946(1)], N3-N6 2.962(1) [3.016(1)].

Two polymorphs were found for diethylammonium 3,5-dinitro-1,2,4-triazolate **12**. When the compound was recrystallized from aqueous solution, the monoclinic polymorph **12a** was obtained, while recrystallization from diethylamine resulted in crystals of the triclinic polymorph **12b**. Both polymorphs consist of $[(H_2NEt_2][DNT])_2$ units in which are formed through four hydrogen bonds between two diethylammonium cations and two DNT anions. One such unit is depicted in Figure 12.

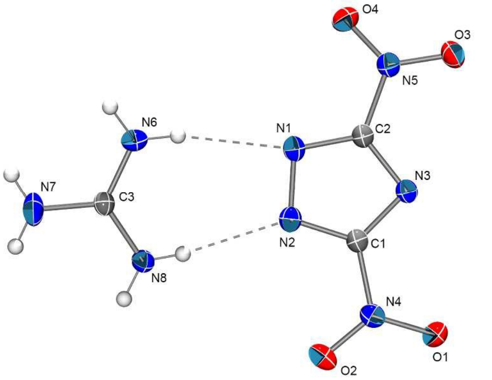


Figure 13: Asymmetric unit in the crystal structure of guanidinium salt **13** with hydrogen bonding. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. For clarity, only some of the observed hydrogen bonds are included. Selected atomic distances (Å): N1-N6 3.044(2), N2-N8 2.897(2).

Guanidinium 3,5-dinitro-1,2,4-triazolate **13** crystallizes in the monoclinic space group $C2/c$ with eight formula units per unit cell. Selected crystallographic parameters of the structure are listed in Table 3. As has already been observed for the ammonium salt $\mathbf{10}\cdot 2H_2O$, the solid-state packing in **13** is defined by strong hydrogen bonding between the guanidinium cations and the anions (Figure 13).

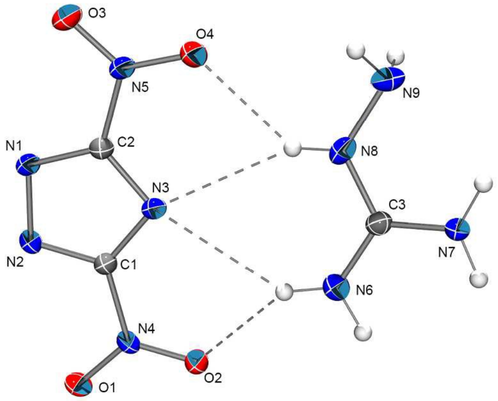


Figure 14: Asymmetric unit in the crystal structure of aminoguanidinium salt **14** with hydrogen bonding. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. For clarity, only the major component of the two disordered anion orientations and only some of the observed hydrogen bonds are included. Selected atomic distances (Å): N3-N6 3.354(7), N3-N8 3.374(6), N6-O2 2.901(6), N8-O4 2.916(5).

The aminoguanidinium salt **14** crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell. Similarly to the guanidinium salt **12**, the solid-state structure is dominated by strong hydrogen bonding between the aminoguanidinium cations and the anions (Figure 14). In the structure, a positional disorder was observed in which the anion is split (ratio 9:1) between two orientations related by a two-fold rotation. Selected crystallographic parameters of the structure are listed in Table 3.

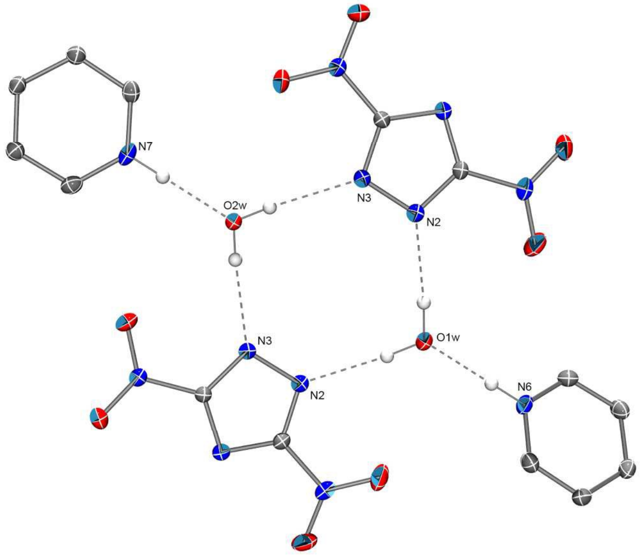


Figure 15: Hydrogen bonding in the pyridinium salt $[HPy][DNT]\cdot H_2O$ $\mathbf{15}\cdot H_2O$. Thermal ellipsoids are shown at the 50% probability level. Some hydrogen atoms have been omitted for clarity. The positions of shown hydrogen atoms were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected atomic distances (Å): N2-O1w 2.861(1), N3-O2w 2.900(1), N6-O1w 2.624(1), N7-O2w 2.666(1).

Pyridinium 3,5-dinitro-1*H*-1,2,4-triazolate **15** crystallizes with one molecule of water per formula unit in the monoclinic space group *C*2/*c*. The solid-state structure consist of $[(HPy][DNT]\cdot H_2O)_2$ units that are arranged in sheets that are coplanar to the *ab* plane of the crystal. One such unit is depicted in Figure 15.

In each unit, two water molecules bridge two DNT anions through hydrogen bonds. For these bonds, the oxygen atom of the water molecules act as hydrogen donors with a nitrogen atom of a triazole ring as acceptor. In addition, the two water oxygen atoms act as hydrogen acceptors in additional hydrogen bonds to pyridinium cations. It is interesting to note that the pyridinium cations of such a unit are not coplanar. The angle between the two planes containing the two six-membered rings is 28.7(1)°.

The solid-state structure of the 5-aminotetrazolium salt $[CH_2N_5][DNT]\cdot H_2O$ **16** is dominated by hydrogen bonds. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with eight formula units in the unit cell. The structure contains chains of alternating cation and anion units that are bridge by hydrogen bonds. The chains are oriented along the *c*-direction of the crystal. While the triazolyl rings of the anions within a chain are co-planar, the planes containing the tetrazolyl rings of the cations are rotated from each other by 73.5(1)°. The angles between the planes of the five-membered rings of the cations and anions are 52.0(1) and 54.8(1)°. The chains are bridged through hydrogen bonds by water molecules. Parts of two such interconnected chains are depicted in Figure 16.

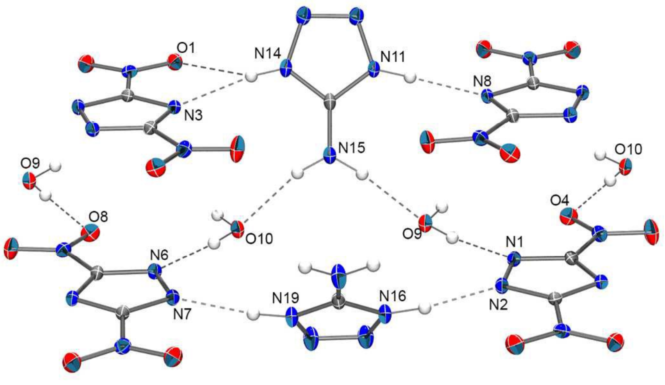


Figure 16: Hydrogen bonding in the 5-aminotetrazolium salt $[CH_2N_5][DNT]\cdot H_2O$ **16**$\cdot H_2O$ bridges two cation-anion chains. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. For clarity, only some of the observed hydrogen bonds are included. Selected atomic distances (Å): N1-O9 2.895(2), N2-N16 2.737(2), N3-N14 2.890(2), N6-O10 2.870(2), N7-N19 2.748(2), N8-N11 2.835(2), N14-O1 3.281(2), O4-O10 2.922(2), O8-O9 2.921(2).

The salts $[PPh_4][DNT]$ **17**, [PPN][DNT] **18**, and $[NMe_4][DNT]$ **19** form crystals that do not contain incorporated water molecules. Selected crystallographic data for compounds **17**-**19** are listed in Table 4. The molecular structures of compounds **17** and **18** are given in the Electronic Supplementary Information. Figure 17 gives the molecular structure of $[NMe_4][DNT]$ (**19**).

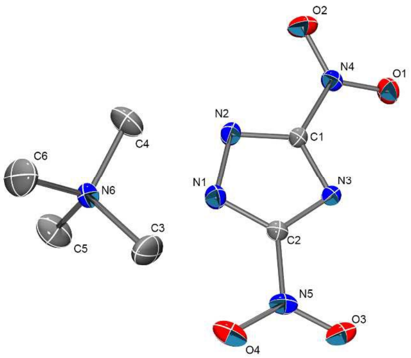


Figure 17: Molecular structure of the NMe_4^+ salt **19**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

The solid-state structures of the PPh_4^+, PPN^+ and NMe_4^+ salts consist of well-separated cations and DNT^- anions. The tetraphenylphosphonium compound **17** crystallizes with four formula units in space group $P2_1/c$. The shortest cation-anion distance in the PPh_4^+ salt was found at 3.188(2) Å (C7-O3). The bis(triphenylphosphine)iminium salt **18** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The shortest distances between the $[(PPh_3)_2N]^+$ cations and DNT^- anions are 3.163(3) Å (C8-O4). The closest anion-anion distance is 5.694(3) Å (N1-N2).

Table 4: Crystallographic data for the $[PPh_4]^+$, $[(PPh_3)_2N]^+$, and $[NMe_4]^+$ DNT salts **17**-**19**.

	17	**18**	**19**
formula	$C_{26}H_{20}N_5O_4P$	$C_{38}H_{30}N_6O_4P_2$	$C_6H_{12}N_6O_4$
mol wt [g/mol]	497.44	696.62	232.22
temp [K]	100(2)	100(2)	100(2)
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	11.2261(5)	10.9099(7)	6.1515(3)
b [Å]	15.0086(7)	11.9031(8)	17.1906(10)
c [Å]	13.8078(6)	14.4603(10)	9.8599(5)
α [deg]	90	112.6130(8)	90
β [deg]	95.0410(10)	90.0610(9)	92.6300(10)
γ [deg]	90	103.5780(9)	90
V [Å^3]	2317.45(18)	1676.28(19)	1664.0(6)
Z	4	2	4
λ [Å]	0.71073	0.71073	0.71073
ρ_{calc} [g/cm^3]	1.426	1.380	1.481
μ [mm^{-1}]	0.164	0.182	0.124
F(000)	1032	724	488
reflns collected	50180	10859	3159
ind reflns	5872	7529	3159
R_{int}	0.0558	0.0198	0.0146
no. of parameters	325	451	184
R_1 [I > 2σ(I)]	0.0373	0.0463	0.0406
[I > 2σ(I)]	0.0837	0.1150	0.1086
GOF	1.010	1.025	1.096

Tetramethylammonium 3,5-dinitro-1,2,4-triazolate **19** crystallizes in space group $P2_1/c$. While the solid-state structure of the $[NMe_4]^+$ salt is still composed of individual $[NMe_4]^+$ and $[DNT]^-$ ions, the ions are not as well separated as in the $[PPh_4]^+$ or $[PPN]^+$ salts. The shortest cation-anion distance is 2.935(2) Å (C3-O1) and the shortest anion-anion distance is 3.083(2) Å (C1-O3). The smaller distances between the ions is due to the smaller size of the $[NMe_4]^+$ cation in comparison to $[PPh_4]^+$ or $[PPN]^+$. On one occasion, a crystalline sample of the composition $[NMe_4][DNT]\cdot HDNT$ was obtained from an impure sample of [TMA][DNT] **19** that contained unreacted HDNT. The molecular structure of $[NMe_4][DNT]\cdot HDNT$ and the full crystallographic data are given in the Electronic Supplementary Information.

Stability of the Compounds

The impact and friction sensitivities of the tetrazolates of this study were determined using a BAM Fall Hammer and BAM Friction Tester, respectively. The obtained sensitivities are summarized in Table 5. Most compounds prepared in this study can be considered insensitive. Only the metal salts **4-8** have measurable friction sensitivities ranging from 160 for CsDNT to 324 N for the Sr^{2+} salt. The metal salts **4-9**, the aminotetrazolium salt **16** and the tetramethylammonium salt **19** had measurable impact sensitivities ranging from the low value of 4.5 J for AgDNT to 85 J for the 5-aminotetrazolium salt. The two silver salts **8** and **9** can be considered highly impact sensitive with determined sensitivities of 4.5 and 10 J, respectively. With impact sensitivities below 39 J, the RbDNT **4**, CsDNT **5**, AgDNT **8**, and $Ag(NH_3)DNT$ **9** must be considered hazardous explosive materials. The thermal stabilities of all compounds of this study were determined using Differential Thermal Analysis (DTA) scans with a heating rate of 5 °C min^{-1}. The results of these scans are summarized in Table 5. Compounds **11, 12**, **15**, and **17-18** melt without decomposition. Melting points ranged from 100 °C for the $[HNEt_3]^+$ salt to 225 °C for the TMA salt.

Table 5: Sensitivity and stability data for the DNT salts studied.

Compound		m.p. [°C]^a	T_{decomp} [°C]^a	FS [N]	IS [J]
$LiDNT\cdot 2H_2O$	**1**$\cdot 2H_2O$	-	280	>360	>100
$NaDNT\cdot 2H_2O$	**2**$\cdot 2H_2O$	-	260	>360	>100
$KDNT\cdot 2H_2O$	**3**$\cdot 2H_2O$	-	265	>360	>100
RbDNT	**4**	-	250	192	20
CsDNT	**5**	-	250	160	25
$Sr(DNT)_2\cdot 6H_2O$	**6**$\cdot 6H_2O$	-	290^c	324	55
$Ba(DNT)_2\cdot 11H_2O$	**7**$\cdot 11H_2O$	-	245	192	55
AgDNT	**8**	-	240	192	4.5
$Ag(NH_3)DNT$	**9**	-	245^d	>360	10
$NH_4DNT\cdot 2H_2O$	**10**$\cdot 2H_2O$	-	190	>360	>100
$[HNEt_3]DNT$	**11**	100	190	>360	>100
$[H_2NEt_2]DNT^c$	**12**	150	190	>360	>100
$[C(NH_2)_3]DNT$	**13**	-	200	>360	>100
$[CH_7N_3]DNT$	**14**	-	200	>360	>100
$[C_5H_6N]DNT\cdot H_2O$	**15**	120	160	>360	>100
$[CH_4N_5]DNT\cdot H_2O$	**16**	-	160	>360	85
$[PPh_4]DNT$	**17**	180	350	>360	>100
[PPN]DNT	**18**	150	340	>360	>100
[TMA]DNT	**19**	225	235	>360	75

^{a} DTA onset; ^{b} possible mixture of polymorphs; ^{c} explosion; ^{d} endotherm at 155 °C (loss of NH_3)

Decomposition onset temperatures, as determined by DTA, range from 245 °C to 290 °C for the metal salts. The three ammonium salts **11-13** showed decomposition temperatures of 190 °C while the two guanidinium salts **14** and **15** have slightly higher decomposition temperatures of 200 °C. With decomposition temperatures of 160 °C, the pyridinium salt **15** and the 5-aminotetrazolium salt **16** are thermally least stable among the investigated DNT salts. Not surprisingly, the most stable compounds towards thermal decomposition are the $[PPh_4]^+$ and $[PPN]^+$ salts **17** and **18**. The decomposition temperatures of the two salts are 340 °C and 350 °C, respectively. It is interesting to note that, with a decomposition temperature of 235 °C, the tetramethylammonium salt **19** was found to be thermally less stable than any investigated metal DNT salt. While most investigated compounds showed smooth decompositions in the DTA scans, the aminoguanidinium salt **14** and the 5-aminotetrazolium salt **16**$\cdot H_2O$ exhibited sharp exotherms in the DTA. Only in the case of the strontium salt **6**$\cdot 6H_2O$ was an explosions observed upon heating.

In addition to DTA scans, the decomposition of the metal DNT salts was also investigated in a qualitative way by heating of the neat salts in the flame of a Bunsen burner. In all cases, the salts deflagrated, producing a coloured flames characteristic for the respective metal cation. These salts could be useful for pyrotechnical applications.

Spectroscopy

The nineteen investigated 3,5-dinitro-1,2,4-triazolates have been characterized by vibrational spectroscopy (IR and Raman) and multinuclear NMR spectroscopy (^1H, ^{13}C, ^{14}N, and ^{31}P). The observed frequencies and intensities of the observed vibrational bands as well as the recorded chemical shifts are listed in the Supplementary Information. Besides resonances due to the respective cations, the ^{13}C NMR and ^{14}N NMR spectra show the resonances expected for a dinitro-substituted symmetric 1,2,4-triazolyl anion. The ^{13}C NMR spectra of all investigated DNT salts exhibit one single resonance at 162 to 164 ppm in $(CD_3)_2CO$, CD_3CN, or DMSO-d_6 due to the DNT anion. The most noticeable feature in the ^{14}N NMR spectra of the DNT anion in the various salts is the resonance of the NO_2-groups at -19 to -22 ppm. This resonance is relatively sharp with a line width of about 50 Hz. Two resonances at about -50 ppm ($\nu_{½} \approx 400$ Hz) and -145 ppm ($\nu_{½} \approx 300$ Hz) are observed for the three nitrogen atoms of the triazolyl ring. Besides vibrational bands due to the cation or water, the vibrational spectra of the DNT salts display strong characteristic bands characteristic for the NO_2 groups at around 1550-1530 cm^{-1} and 1520-1480 cm^{-1} (ν_{as} NO_2), as well as 1400-1370 cm^{-1} and 1360-1290 cm^{-1} (ν_s NO_2). In addition, a strong band for the deformation of the C_2N_3 ring is observed in the range 850-820 cm^{-1}. These bands are in good agreement with vibrational data published previously for potassium 3,5-dinitro-1,2,4-triazolate and 1-methyl-3,5-dinitro-1,2,4-triazole.[37, 38] Due to the negative charge, the observed vibrational bands of the DNT anion are shifted by 10-40 cm^{-1} to lower wavenumbers in comparison to the neutral parent compound 3,5-dinitro-1*H*-1,2,4-triazole (HDNT, see Electronic Supplementary Information). The effect is most pronounced for the two asymmetric stretch modes (in-phase and out-of-phase) of the NO_2 groups bands at 1550-1530 cm^{-1} and 1520-1480 cm^{-1} (HDNT: 1563 and 1530 cm^{-1}).

Conclusions

Numerous salts of 3,5-dinitro-1*H*-1,2,4-triazole have been prepared. Most of the studied 3,5-dinitro-1,2,4-triazolates have relatively high thermal stability and show only very low shock and friction sensitivity. The salts containing alkali metal, alkali earth metal, and silver cations exhibit coloured emissions upon combustion and might be of interest as components in pyrotechnics formulations. Most compounds in this study have been fully characterized by their X-ray crystal structure, vibrational and multinuclear NMR spectra, their decomposition temperature, as well as friction and impact sensitivities.

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Notes and references

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Electronic Supplementary Information (ESI) available: Detailed experimental descriptions, vibrational data for HDNT, and crystallographic reports including packing diagrams. See DOI: 10.1039/b000000x/

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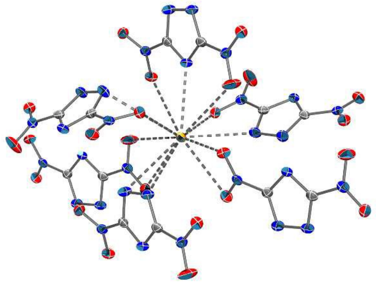
Table of Content

Several novel salts with the energetic 3,5-dinitro-1,2,4-triazolate (DNT) anion have been prepared and characterized.



RbDNT