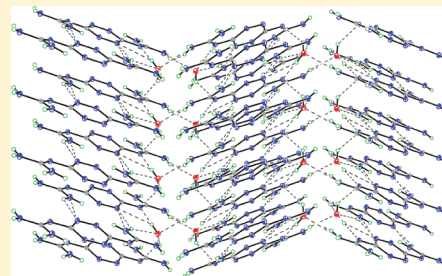


Two High Nitrogen Content Energetic Compounds: 3,6-Diguanidino-1,2,4,5-Tetrazine and Its Dipерchlorate

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ABSTRACT: High nitrogen content energetic compounds 3,6-diguanidino-1,2,4,5-tetrazine [(DGTz)(H₂O)₂] and its dipерchlorate [(DGTz)(ClO₄)₂] were prepared and characterized by elemental analysis and Fourier transform infrared (FT-IR) spectroscopy. Their crystal structures were determined by applying X-ray single crystal diffraction. The hydrogen atoms in the 3- and 6-sites of the tetrazine heterocycle have been disubstituted by guanidine groups for (DGTz)(H₂O)₂, and two crystal water molecules were present. In the (DGTz)(ClO₄)₂ molecule, two ClO₄⁻ and one DGTz²⁺ groups were bonded together by electrostatic attraction and hydrogen bonds. The thermal decomposition process of the two compounds was investigated through differential scanning calorimetry (DSC) and thermogravimetric/differential analysis (TG-DTG). The results of the decomposition are nearly gaseous products. The kinetic parameters of the exothermic process were calculated by using Kissinger's and Ozawa–Doyle's methods.



■ INTRODUCTION

High nitrogen content heterocyclic compounds have attracted increased attention of the chemists all over the world in recent times due to their impressive performance in the area of advanced high-energy materials aimed at military and civilian needs.^{1–12} Unlike conventional energetic materials which get their energy from the oxidation fracture of C–H bonds, high nitrogen content compounds have a large amount of N–N and C–N bonds and therefore possess large positive heats of formation, so they derive most of their energy from the transformation of the bonds between N-atoms. Such transformations are accompanied by an enormous energy release due to the wide difference in the average bond energies of N–N (160 kJ·mol⁻¹) and N=N (418 kJ·mol⁻¹), compared to that of N≡N (954 kJ·mol⁻¹). Nitrogen heterocyclic triazole,^{9,13–23} tetrazole,^{1,3,4,17,20–22,24–28} tetrazine,^{29–33} and their monosubstitute or multisubstitute derivatives have gained a large amount of interest as preeminent energetic materials and are widely used in some areas.

1,2,4,5-Tetrazine with the nitrogen content of 63.8 % is a common parent compound in the area of energetic materials synthesis.^{34–39} The 3- and 6-sites of the tetrazine ring have high activity and can be easily substituted by some nucleophiles to generate various derivatives.³³ To enhance the content of nitrogen and make its structure and properties more varied, some nitrogen-rich groups with explosive properties were brought in, such as amino,⁴⁰ hydrazino,³⁰ azido,²⁹ guanidino,^{15,32,41–43} nitro-guanidino, and 1*H*-1,2,3,4-tetrazol-5-ylamino groups.^{31,44} These compounds exhibit promising applications in the areas of insensitive high-energy explosives, low signature propellants, gas generating compositions, pyrotechnic compositions, and high-performance, environmentally friendly fireworks.

Chavez and co-workers synthesized 3,6-diguanidino-1,2,4,5-tetrazine [(DGTz)(H₂O)₂] in 2004³² through the reaction of 3,6-bis(3,5-dimethyl-pyrazole)-1,2,4,5-tetrazine (BT) and guanidine and prepared the dipерchlorate and dinitrate salts of DGTz, with a detailed investigation of their interesting explosive performance and extraordinary combustion properties. In 2006, Wang et al. studied improvements in the synthesis of DGTz and its dipерchlorate and dinitrate salts and the reaction of triaminoguanidine nitrate and diacetylmethane after condensation, oxidation, and neutralization.⁴¹ Although some research has been completed on DGTz and its dipерchlorate salts, their crystal structures were not obtained until our recent works.

To investigate the structure and properties of DGTz in detail and explore new DGTz based high nitrogen content energetic compounds, we prepared the title compounds and reported their crystal structures, thermal decomposition, and non-isothermal kinetics analysis.

■ EXPERIMENTAL SECTION

Caution. 3,6-Diguanidino-1,2,4,5-tetrazine and its dipерchlorate are energetic materials and tend to explode under certain conditions. Appropriate safety precautions should be taken, especially when these compounds are prepared on a large scale.

Materials and Instruments. All chemical reagents and solvents of analytical grade were bought from Beijing Chemical Reagent Co. and used as supplied. Triaminoguanidine monohydrochloride used to prepare BT was purchased

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Table 1. Crystal Data and Structure Refinement for (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂

	(DGTz)(H ₂ O) ₂	(DGTz)(ClO ₄) ₂
empirical formula	C ₄ H ₈ N ₁₀ ·2H ₂ O	C ₄ H ₁₀ N ₁₀ Cl ₂ O ₈
formula mass	232.24	397.12
temperature (K)	103	93
crystal size (mm)	0.02 × 0.07 × 0.37	0.05 × 0.05 × 0.43
crystal system	monoclinic	monoclinic
space group	C2/c	P21/c
Z	4	2
a (nm)	1.3077(5)	0.48581 (15)
b (nm)	0.36935(14)	1.3058 (4)
c (nm)	1.9823(8)	1.0519(3)
β (deg)	95.158(7)	91.159(5)
cell volume (nm ³)	0.9536(6)	0.6672(3)
density, calculated (g·cm ⁻³)	1.618	1.977
μ (mm ⁻¹)	0.132	0.559
F(000)	488	404
θ (deg)	3.1 to 27.5	3.1 to 27.5
h, k, and l range	-16 to 16, -4 to 4, -25 to 25	-6 to 6, -16 to 16, -13 to 13
reflection collected	4354	6551
independent reflection (R _{int})	1092 [0.028]	1530 [0.036]
refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²
data/restraint/parameter	1092/0/97	1530/0/129
goodness-of-fit on F ²	0.996	0.999
final R ₁ and wR ₂ [I > 2σ(I)]	R ₁ = 0.0417, wR ₂ = 0.1005 ^a	R ₁ = 0.0593, wR ₂ = 0.1302 ^b
R ₁ and wR ₂ indices (all data)	R ₁ = 0.0537, wR ₂ = 0.1081 ^a	R ₁ = 0.0675, wR ₂ = 0.1338 ^b
Δρ _{max} Δρ _{min} (e·nm ⁻³)	241, -206	517, -443

^aw = 1/[σ²(F_o²) + (0.0669p)² + 0.4590p], where p = (F_o² + 2F_c²)/3. ^bw = 1/[σ²(F_o²) + (0.0631p)² + 0.3600p], where p = (F_o² + 2F_c²)/3.

Table 2. Selected Bond Lengths (nm) and Bond Angles (deg) for (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂

(DGTz)(H ₂ O) ₂ ^a		(DGTz)(ClO ₄) ₂ ^b		(DGTz)(ClO ₄) ₂ ^b	
Bond Lengths					
N(1)–N(2)	0.13206(18)	Cl(1)–O(4)	0.14463(17)	N(2)–C(1)	0.1339(3)
N(1)–C(1)#1	0.1351(2)	Cl(1)–O(3)	0.14399(17)	N(3)–C(1)	0.1381(3)
N(2)–C(1)	0.1355(2)	Cl(1)–O(1)	0.14472(17)	N(1)#1–C(1)	0.1347(3)
N(3)–C(1)	0.13672(19)	Cl(1)–O(2)	0.14484(17)	N(1)–N(2)	0.1318(3)
N(3)–C(2)	0.13373(19)	N(3)–C(2)	0.1366(3)		
N(4)–C(2)	0.1348(2)	N(4)–C(2)	0.1314(3)		
N(5)–C(2)	0.1326(2)	N(5)–C(2)	0.1318(3)		
Bond Angles					
N(1)–N(2)–C(1)	118.58(12)	O(3)–Cl(1)–O(4)	110.07(10)	N(2)–N(1)–C(1)#1	116.76(19)
C(1)–N(3)–C(2)	112.51(12)	O(1)–Cl(1)–O(4)	108.81(9)	N(1)–N(2)–C(1)	117.09(19)
N(2)–N(1)–C(1)#1	118.89(12)	O(1)–Cl(1)–O(2)	109.08(9)	C(2)–N(3)–C(2)	129.2(2)
N(2)–C(1)–N(3)	123.99(13)	O(1)–Cl(1)–O(3)	110.20(10)	N(2)–C(1)–N(3)	120.4(2)
N(1)#1–C(1)–N(2)	122.53(13)	O(2)–Cl(1)–O(3)	109.93(10)	N(3)–C(2)–N(4)	117.1(2)
N(1)#1–C(1)–N(3)	113.47(12)	N(1)#1–C(1)–N(2)	126.1(2)	N(3)–C(2)–N(5)	121.1(2)
N(3)–C(2)–N(4)	116.92(13)	N(1)#1–C(1)–N(3)	113.5(2)		
N(3)–C(2)–N(5)	125.94(13)	N(4)–C(2)–N(5)	121.8(2)		
N(4)–C(2)–N(5)	117.14(14)	O(2)–Cl(1)–O(4)	108.72(9)		

^aSymmetry transformations used to generate equivalent atoms for (DGTz)(H₂O)₂: #1 1 - x, 1 - y, 1 - z. ^bSymmetry transformations used to generate equivalent atoms for (DGTz)(ClO₄)₂: #1 2 - x, 1 - y, 1 - z.

commercially. BT was prepared according to the literature⁴² and obtained as a red solid with a yield of 88 %.

Elemental analyses were performed on a flash EA 1112 full-automatic trace element analyzer. The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellet) in the range of (4000 to 400) cm⁻¹ with the resolution of 4 cm⁻¹. Differential scanning calorimetry (DSC) was carried out on a model Pyris-1 differential scanning calorimeter in static air. Thermogravi-

metric (TG) analysis were carried out on a model Pyris-1 thermogravimeter analyzer using dry oxygen-free nitrogen as atmosphere with a flowing rate of 20 mL·min⁻¹. The sample of about 0.5 mg was sealed in aluminum pans for DSC and held in platinum pans for TG.

Synthesis. Methanol (100 mL), sodium methoxide (4.5 g), and guanidine nitrate (6.2 g, 0.05 mol) are stirred for 30 min at room temperature. BT is added in one portion and stirred at room temperature for 10 h. The red precipitate is collected by

filtration, washed with water, and transferred to a beaker; 70 % perchloric acid (32 mL) is added with stirring, and a few minutes later (DGTz)(ClO₄)₂ was precipitated and filtrated. (DGTz)(ClO₄)₂ (10 g, 0.025 mol) is stirred in water (200 mL) and sodium hydroxide (1 mol·L⁻¹) for 24 h, and (DGTz)(H₂O)₂ is filtered, washed with water, and air-dried. Single crystals of these compounds suitable for X-ray analyses were obtained by slow crystallization from the filtrate. Anal. Calcd. (%) for DGTz: C 24.49, H 4.08, N 71.43; Found (%): C 24.50, H 4.05, N 71.45. Yield (based on (DGTz)(ClO₄)₂): 83 %. Anal. Calcd. (%) for (DGTz)(ClO₄)₂: C 12.09, H 2.50, N 35.45; Found (%): C 12.11, H 2.70, N 35.46. Yield (based on BT): 44 %.

X-ray Crystallography. A Rigaku AFC-10/Saturn 724+ CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.071073$ nm) was applied for structure analyses of the title compounds. The data were collected at 103 K for (DGTz)(H₂O)₂ and 93 K for (DGTz)(ClO₄)₂ using φ and ω scan modes. The programs SHELXS-97^{45,46} and SHELXL-97⁴⁷ were used for structure determination and refinement. The structures were solved by direct methods, and all non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least-squares on F^2 . All hydrogen atoms were generated geometrically, assigned appropriated isotropic thermal parameters, and included in structure factor calculations. Crystallographic data and experimental details for structure analyses are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2, and the hydrogen bond lengths and angles are listed in Table 3. Further information concerning the crystal-structure

Table 3. Hydrogen Bond Lengths (Å) and Angles (deg) for (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂

D—H...A	D—H	H...A	D...A	D—H...A
(DGTz)(H ₂ O) ₂ ^a				
O(1)—H(1A)...N(3)	0.091(2)	0.193(2)	0.2833(2)	172(2)
O(1)—H(1A)...N(1) #1	0.091(2)	0.262(2)	0.3266(2)	128.4(18)
O(1)—H(1B)...N(3) #5	0.088(3)	0.230(3)	0.3047(2)	142(2)
N(4)—H(4A)...O(1) #4	0.090(2)	0.225(2)	0.3089(2)	154.8(16)
N(4)—H(4B)...O(1) #3	0.084(2)	0.217(2)	0.2942(2)	153(2)
N(5)—H(5A)...N(1) #4	0.083(2)	0.240(2)	0.3152(2)	150.5(17)
N(5)—H(5A)...N(1) #2	0.083(2)	0.2405(19)	0.2950(2)	123.8(16)
N(5)—H(5B)...N(2)	0.0889(19)	0.1998(19)	0.2675(2)	131.9(16)
(DGTz)(ClO ₄) ₂ ^b				
N(3)—H(3)...O(2)	0.080(3)	0.207(3)	0.2865(3)	170(3)
N(4)—H(4A)...O(3)	0.077(3)	0.229(3)	0.3052(3)	174(3)
N(4)—H(4B)...O(4) #3	0.083(3)	0.216(3)	0.2978(3)	168(2)
N(5)—H(5A)...N(2)	0.090(3)	0.209(3)	0.2733(3)	128(2)
N(5)—H(5A)...O(1) #2	0.090(3)	0.245(3)	0.2975(3)	117(2)
N(5)—H(5B)...O(1) #3	0.085(3)	0.219(3)	0.3033(3)	172(3)

^aSymmetry transformations used to generate equivalent atoms for (DGTz)(H₂O)₂: #1: 1 - x, 1 - y, 1 - z; #2: 3/2 - x, 1/2 - z, 1 - z; #3: 1 - x, y, 1/2 - z; #4: 1/2 + x, -1/2 + y, z; #5: x, 1 + y, z.
^bSymmetry transformations used to generate equivalent atoms for (DGTz)(ClO₄)₂: #2: 2 - x, 1 - y, 1 - z; #3: 1 + x, 3/2 - y, -1/2 + z.

determinations in CIF format is available from the Cambridge Crystallographic Data Centre (CCDC 816407 and 816408; http://www.ccdc.cam.ac.uk/data_request/cif; Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Infrared Spectra. Infrared spectroscopy was applying to identify the structure of the title compounds. The bonds at (3399 and 3297) cm⁻¹ are assigned to the stretching vibrations of the NH₂ groups for (DGTz)(H₂O)₂, and the corresponding bonds at (3400 and 3232) cm⁻¹ are found for (DGTz)(ClO₄)₂. The bonds at (3094 and 3095) cm⁻¹ are assigned to the stretching vibrations of the imino groups for (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂, respectively. The frameworks of tetrazine are confirmed at (1429 and 928) cm⁻¹ for (DGTz)(H₂O)₂ and (1424 and 936) cm⁻¹ for (DGTz)(ClO₄)₂. The characteristic absorption peaks of perchlorate ion for (DGTz)(ClO₄)₂ can be found at (1076, 690, and 626) cm⁻¹.

Structure Description. DGTz was obtained by two guanidino substitution of the 3-H and 6-H of 1,2,4,5-tetrazine. As displayed in the molecular structure of (DGTz)(H₂O)₂ shown in Figure 1, two lattice water molecules were present.

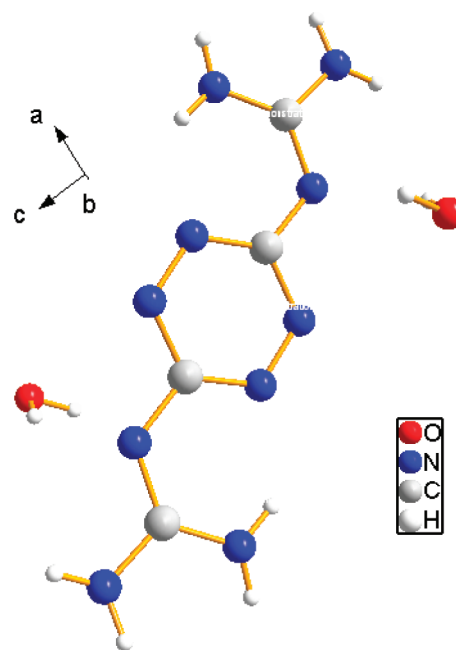


Figure 1. Molecular unit of (DGTz)(H₂O)₂.

Figure 2 shows the molecular unit of (DGTz)(ClO₄)₂. There are two ClO₄⁻ and one DGTz²⁺ cations in the (DGTz)(ClO₄)₂ molecule; they were bonded together by electrostatic attraction. Two hydrogen protons from two HClO₄ molecules transfer to the DGTz molecule; N(5) and N(5A) accepted the hydrogen protons to form the bivalent DGTz²⁺ cation.

In the (DGTz)(H₂O)₂ molecule, the C—N bond lengths range from 0.1326(2) nm (N(5)—C(2)) to 0.13672(19) nm (N(3)—C(1)) with an average value of 0.13467 nm, which is 0.0076 nm longer than the normal C=N bond length (0.1270 nm) and 0.0104 nm shorter than the normal C—N bond length (0.1450 nm).⁴⁸ The N—N bond distance is 0.13206(18) nm, longer than the normal N=N bond length

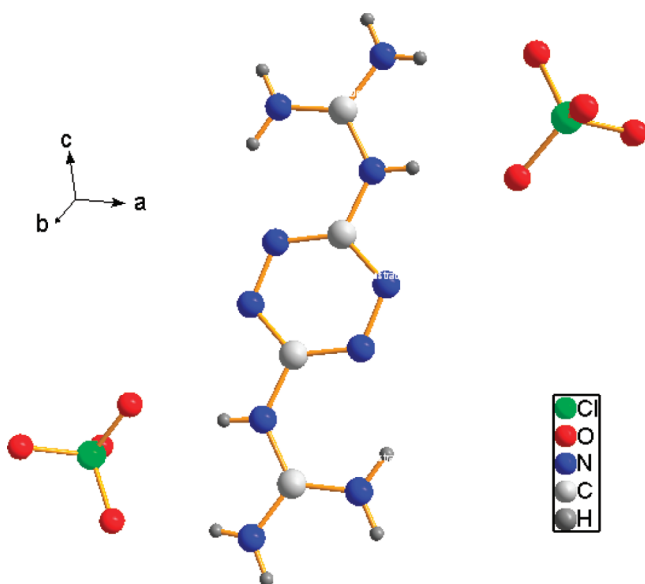


Figure 2. Molecular unit of $(\text{DGTz})(\text{ClO}_4)_2$.

of 0.1252 nm and shorter than the normal N—N bond length of 0.1470 nm.⁴⁸ For $(\text{DGTz})(\text{ClO}_4)_2$, the lengths of C—N bond are in the range of 0.1314(3) nm (C(2)—N(4)) to 0.1381(3) nm (C(1)—N(3)) with an average of 0.13428 nm. These values fall between the C—N single bond distance (0.1450 nm) and the C=N double bond distance (0.1270 nm). The distance of N(1)—N(2) is 0.1318(3) nm, longer than the normal N=N bond length of 0.1252 nm and shorter than the normal N—N bond length of 0.1470 nm.⁴⁸ The bond angles of the tetrazine ring of the DGTz^{2+} have a minimum of $116.76(19)^\circ$ for N(2)—N(1)—C(1)#1, a maximum of $126.1(2)^\circ$ for N(1)#1—C(1)—N(2), and an average of 121.43° . It could be concluded that the conjugation effect leads to a special π bond among the C=N, C—N, and N=N bonds. These facts imply the existence of the delocalization effect, making the whole compound molecular energy decrease and improving the thermal stability of both compounds. The bond lengths and angles of the disubstituted guanidine-tetrazine in the $(\text{DGTz})(\text{ClO}_4)_2$ molecule are similar to $(\text{DGTz})(\text{H}_2\text{O})_2$. In the disubstituted guanidine-tetrazine, all non-hydrogen atoms are coplanar for both title compounds. All of the planes of guanidine-tetrazines are arranged in two different orientations, as shown in Figure 3.

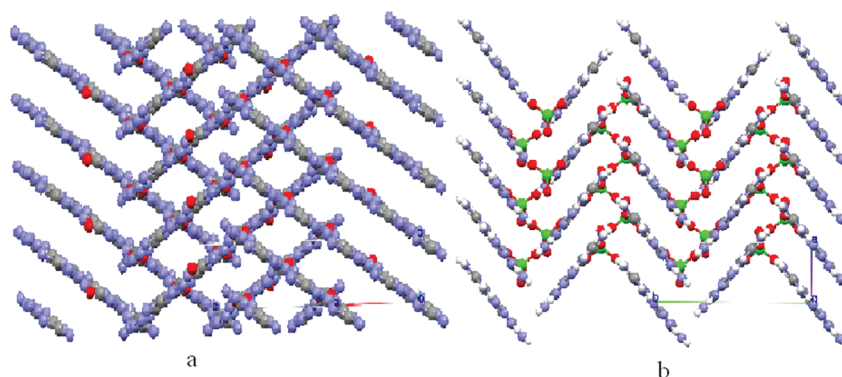


Figure 3. Planes of guanidine-tetrazine arranged in two different orientations for $(\text{DGTz})(\text{H}_2\text{O})_2$ (a) and $(\text{DGTz})(\text{ClO}_4)_2$ (b).

In the $(\text{DGTz})(\text{H}_2\text{O})_2$ and $(\text{DGTz})(\text{ClO}_4)_2$ compounds, all of the molecular units were linked together into three-dimensional network structures by the extensive intramolecular and intermolecular hydrogen bonds, due to the existence of the nitrogen atoms from guanidine-tetrazine and oxygen atoms from the lattice water molecules or perchlorate anions. Figures 4 and 5 are the packing diagrams of $(\text{DGTz})(\text{H}_2\text{O})_2$ in crystal

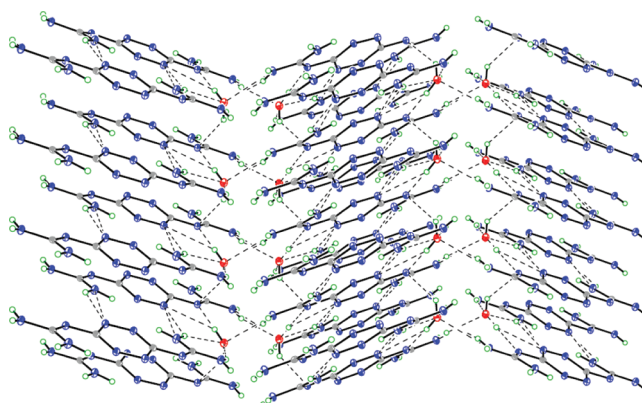


Figure 4. Packing diagram of $(\text{DGTz})(\text{H}_2\text{O})_2$ viewed along the a -axis.

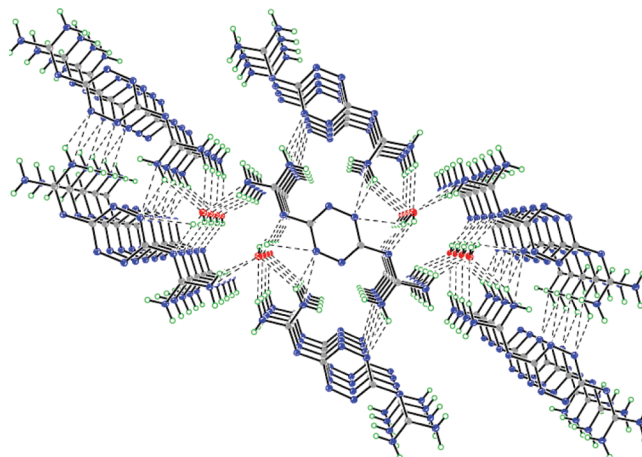


Figure 5. Packing diagram of $(\text{DGTz})(\text{H}_2\text{O})_2$ viewed along the b -axis.

viewed along the a -axis and b -axis, respectively. From the packing diagrams, we can see the abundant H-bonds connecting the molecule together to a stable structure. When constructing the fascinating architecture, one H_2O connected

three guanidine-tetrazine molecules via the H-bonds of between O(1) and N(3) or N(4). Moreover, in the DGTz molecules, intramolecular and intermolecular hydrogen bonds were formed among N(1), N(2), and N(5). Around each guanidine-tetrazine molecule, there are six H₂O molecules and a large amount of H-bonds. The packing diagrams of (DGTz)(ClO₄)₂ in crystal viewed along the *a*-axis and *b*-axis are shown in Figures 6 and 7, respectively. In the (DGTz)-

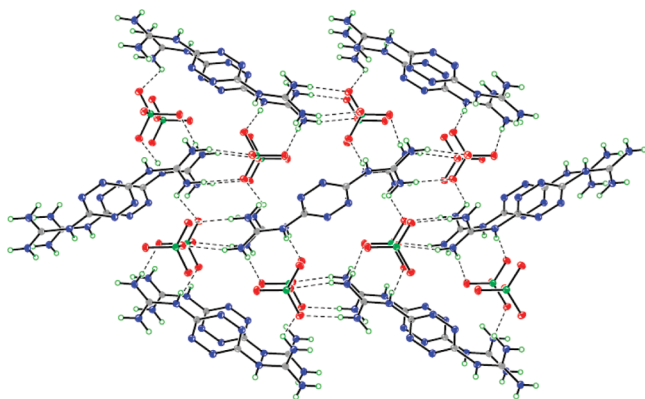


Figure 6. Packing diagram of (DGTz)(ClO₄)₂ viewed along the *a*-axis.

(ClO₄)₂ molecule, a laminar structure was formed in the plane of *b*-axis × *c*-axis as shown in the packing diagram viewed along the *b*-axis. The distance between the layers is 0.4858 nm, equal to the lattice parameter *a*. Hydrogen bonds in (DGTz)(ClO₄)₂ joined the layers together to a 3-D network. Each ClO₄⁻ joined four adjacent guanidine-tetrazine cations. Around one DGTz cation, there are eight ClO₄⁻ anions. For the two compounds, the H₂O molecules and ClO₄⁻ ions made a vital contribution to the formation of hydrogen bonds and then the stable 3-D architecture.

Thermal Decomposition. To assess the thermal stabilities of (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂, the thermal decomposition processes were investigated by using DSC and TG measurements. Figures 8 and 9 are showing the DSC curves for these compounds at a heating rate of $\beta = 10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, respectively. The TG-DTG curves of the two compounds at a heating rate of $\beta = 10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in N₂ gas flowing at the rate of 20 mL·min⁻¹ were illustrated in Figures 10 and 11. The tested samples are the precipitated powder instead of the crystalline solid, which were dried in a water bath oven at 50 °C to remove any moisture beside crystal water.

The DSC curve of (DGTz)(H₂O)₂ shows that there are two decomposition processes: one endothermic process in the range of 54.3 °C to 98.3 °C with a peak temperature of 79.2 °C, and one sharp exothermic process which begins at 272.8 °C and ends at 310.8 °C with a peak temperature of 297.1 °C.

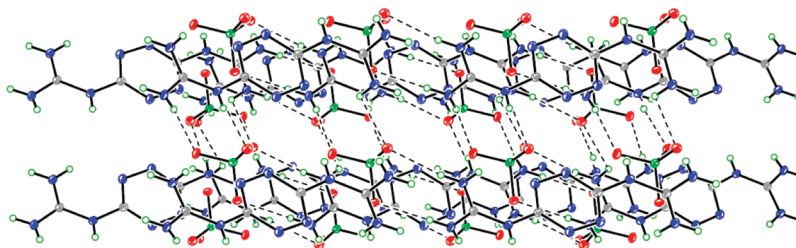


Figure 7. Packing diagram of (DGTz)(ClO₄)₂ viewed along the *b*-axis.

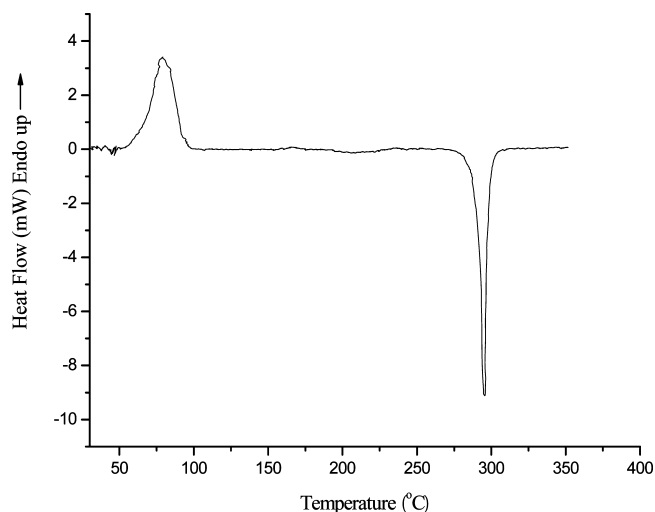


Figure 8. DSC curve of (DGTz)(H₂O)₂ at a heating rate of 10 °C·min⁻¹.

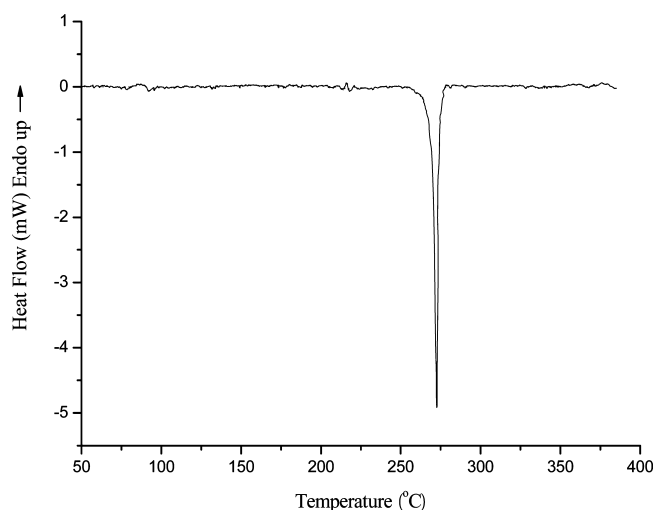


Figure 9. DSC curve of (DGTz)(ClO₄)₂ at a heating rate of 10 °C·min⁻¹.

Meanwhile, in the DSC curve of (DGTz)(ClO₄)₂, there is only one sharp exothermic process from 255.7 °C to 278.1 °C, with the peak temperature of 272.4 °C. The rapid exothermic process in a very short time demonstrated a potential application in the area of ignition. (DGTz)(ClO₄)₂ starts its violent exothermic decomposition at 255.7 °C, which is 17.1 °C lower than (DGTz)(H₂O)₂. Also, (DGTz)(ClO₄)₂ decomposed directly without a melting process unlike (DGTz)(H₂O)₂. These may be attributed to the ionic structure of

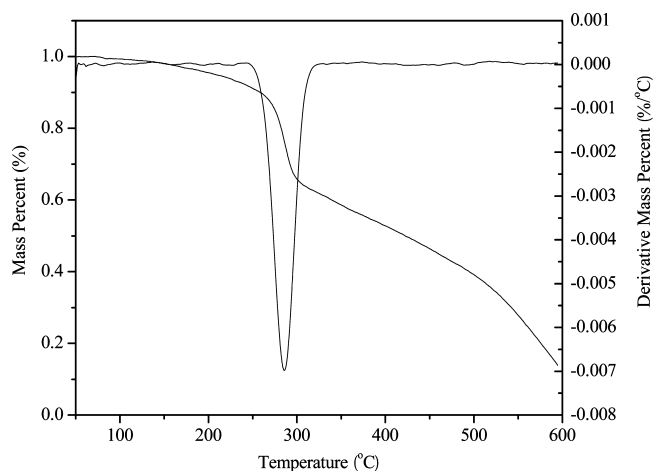


Figure 10. TG-DTG curves of (DGTz)(H₂O)₂ at a heating rate of 10 °C·min⁻¹.

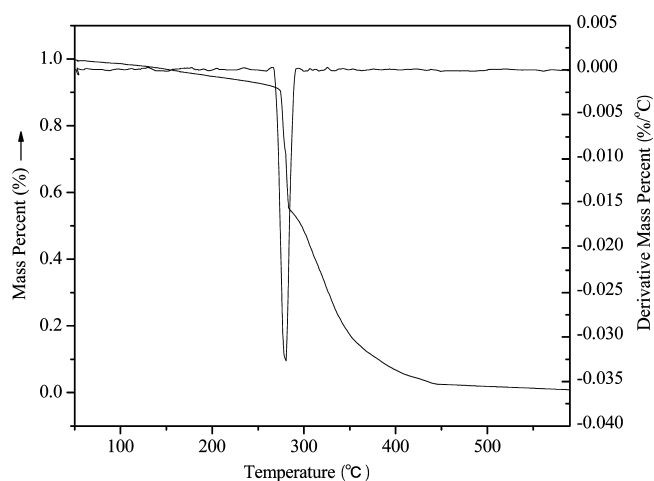


Figure 11. TG-DTG curves of (DGTz)(ClO₄)₂ at a heating rate of 10 °C·min⁻¹.

(DGTz)(ClO₄)₂ and the strong oxidizing property of the perchlorate ion.

The TG-DTG curves of the two compounds shown that there are two stages in the process of thermal decomposition. The first mass loss stage occurs in the range of (247.0 to 323.4) °C with a mass loss of 38 % of the initial mass for (DGTz)(H₂O)₂. For (DGTz)(ClO₄)₂, the first stage of mass loss of 49.7 % was in the temperature range of 263.0 °C to 294.9 °C. This decomposition process is attributed to the breakdown of the amino groups in DGTz and the tetrazine rings. The second stage of both the two compounds is a slow process of thermal decomposition with continuous mass loss, and the final residue at 600 °C amounts to 1 % of the initial mass for (DGTz)(H₂O)₂ and left nothing for (DGTz)(ClO₄)₂. The title compounds mainly contain C, H, and N; we can calculate that the majority of products of decomposition are N₂ and other gaseous products.

Nonisothermal Kinetic Analysis. In the present work, Kissinger's method⁴⁹ and Ozawa–Doyle's method⁵⁰ are widely used to determine the apparent activation energy (*E*) and the

pre-exponential factor (*A*). The Kissinger (1) and Ozawa–Doyle (2) equations are as follows, respectively:

$$\frac{d\ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R} \quad (1)$$

$$\log \beta + \frac{0.4567E_a}{RT_p} = C \quad (2)$$

where *T_p* is the peak temperature, °C; *R* is the gas constant, 8.314 kJ·mol⁻¹·°C⁻¹; *β* is the linear heating rate, °C·min⁻¹; *C* is a constant.

We can infer that the only exothermic process makes a dominant effect on the decomposition of the title compound from the DSC and TG curves of (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂. Based on the DSC curves obtained under the conditions of static air at four different heating rates of (5, 10, 15, and 20) °C·min⁻¹, the values of the peak temperature *T_p* (K), the apparent activation energies *E_k* and *E_o* (kJ·mol⁻¹, where subscript *k* is Kissinger's method and subscript *o* is Ozawa–Doyle's method), the pre-exponential factor *A_k* (S⁻¹), and linear coefficients *R_k* and *R_o* were determined by Kissinger's method and Ozawa–Doyle's method. The detailed data and calculated kinetic parameters are listed in Table 4. The

Table 4. Peak Temperatures of the First Exothermic Stage at Different Heating Rates and the Kinetic Parameters^a

heating rates (°C·min ⁻¹)	(DGTz)(H ₂ O) ₂	(DGTz)(ClO ₄) ₂
	peak temperatures (°C)	peak temperatures (°C)
5	292.1	268.8
10	297.1	272.4
15	304.9	281.9
20	306.4	285.1
<i>E_k</i> (kJ·mol ⁻¹)/ln(<i>A_k</i> /S ⁻¹)/ <i>R_k</i>	228.6/19.02/-0.9756	178.5/15.07/-0.9516
<i>E_o</i> (KJ·mol ⁻¹)/ <i>R_o</i>	226.4/-0.9775	178.5/-0.956

^aSubscript *k*: Kissinger's method; *o*: Ozawa–Doyle's method; *R*: linear correlation coefficient.

calculated results using both methods correspond well with each other, and they are all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials.⁵¹ The apparent activation energy of (DGTz)(H₂O)₂ is about 50 kJ·mol⁻¹ higher than (DGTz)(ClO₄)₂; this reveals that the energy barrier encountered for decomposition of (DGTz)(ClO₄)₂ is smaller and easy to decompose. This corresponds to the onset temperature of the DSC and is caused by the existence of ClO₄⁻.

The Arrhenius equation can be expressed by using the calculated *E_a* (the average of *E_k* and *E_o*) and ln *A_k* (Table 4) as follows: ln *k* = 19.02 - 228.6·10³/RT, ln *k* = 15.07 - 178.5·10³/RT. The equations can be used to estimate the rate constant of the initial decomposition process of (DGTz)-(H₂O)₂ and (DGTz)(ClO₄)₂ and also determine their thermal decomposition mechanism.

Energetic Properties. The energetic property data of (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂ are summarily listed in Table 5. For (DGTz)(ClO₄)₂, it appears that ClO₄⁻ reduced the nitrogen content but increased the oxygen balance and the density. The detonation velocity (*D*) and detonation pressure (*P*) of 3,6-diguanidino-1,2,4,5-tetrazine without crystal water

Table 5. Energetic Properties of (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂

	(DGTz)(H ₂ O) ₂	(DGTz)(ClO ₄) ₂
nitrogen content (%)	60.28	35.25
oxygen balance (%)	-82.67	-20.15
density (g·cm ⁻³)	1.466 (calculated), 1.618 (crystal)	1.977 (crystal)
DSC onset (°C)	273	256
D (m·s ⁻¹)	7708 (calculated), 7310 (experimental) ⁵²	8313 (calculated), 8070 (experimental) ⁵²
P (GPa)	23.1 (calculated), 20.7 (experimental) ⁵²	32.6 (calculated), 31.2 (experimental) ⁵²
impact (cm), ³² 2.5 kg		24
friction (kg), ³² BAM	36	8.6
spark (J) ³²	>0.36	>0.36

molecules was calculated by the Kamlet–Jacobs method based on the theoretical heat of formation and density. Meanwhile, the values of *D* and *P* for (DGTz)(ClO₄)₂ were obtained through an experiential equivalent nitrogen equation with the crystal density. These data can correspond to reported experimental values.⁵² The impact sensitivity of (DGTz)(ClO₄)₂ is approximate to cyclotrimethylene trinitramine (RDX, 24 cm) and tetrahexamine tetranitramine (HMX, 26 cm), much more sensitive than trinitrotoluene (TNT, 200 cm).⁵² The friction sensitivity of (DGTz)(ClO₄)₂ is much sensitive than (DGTz)(H₂O)₂ (36 kg) with a value of 8.6 kg. Both of the two compounds are insensitive to sparking; the values of spark energy for a 50 % probability of initiation (*E*₅₀) are larger than 0.36, whereas the data of HMX (0.21 J) and RDX (0.15 J) are smaller.⁵³

CONCLUSION

(DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂ were prepared and demonstrated by elemental analysis and FT-IR spectroscopy. Their single crystals were obtained for the first time, and the structures were investigated in detail. In the two compounds, H₂O molecules and ClO₄⁻ ions made a vital contribution to the formation of hydrogen bonds and the stable 3-D architecture. Thermal decomposition analysis illustrated that a rapid exothermic process occurs in very short time and a great number of gases was produced. The Arrhenius equations of (DGTz)(H₂O)₂ and (DGTz)(ClO₄)₂ were obtained through nonisothermal kinetic analyses as $\ln k = 19.02 - 228.6 \cdot 10^3 / RT$ and $\ln k = 15.07 - 178.5 \cdot 10^3 / RT$, respectively. The energetic properties and thermal analyses confirmed the potential application of the compounds in the area of energetic materials.

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