Synthesis, Crystal Structure, and Properties of Energetic Complex Magnesium 5,5′-Dinitramino-3,3′-bi[1,2,4-triazolate] Hexahydrate

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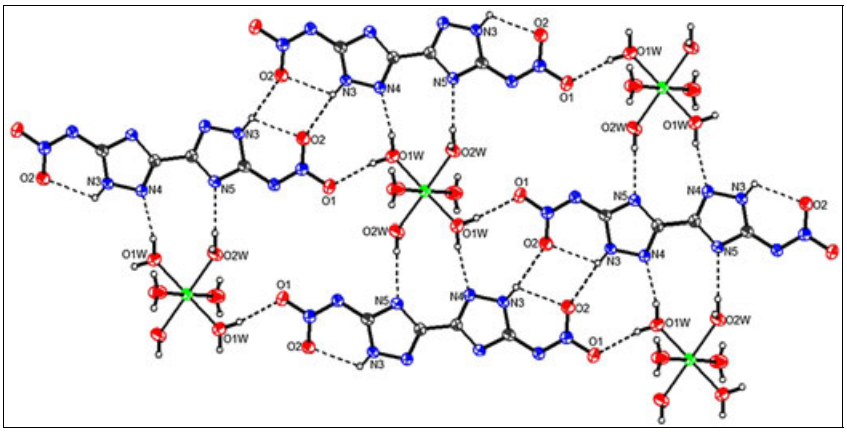

Alkaline Earth metal (Mg) energetic complex with 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] dihydrate (DNABT) has been synthesized and structurally characterized by FTIR spectroscopy, elemental analysis, and single X-ray diffraction. The thermal decomposition processes of the complex and DNABT were studied by means of the TDA-TG technologies. Sensitivity tests reveal that the complex is more insensitive to mechanical stimuli than DNABT. Combustion behavior shows that **1** has good color performances.

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INTRODUCTION

The continuous search for safe (insensitive, highly tolerant to various external perturbations) and powerful (releasing much energy on demand) energetic materials is an exciting and challenging area of physical chemistry. In many cases, high performance and low sensitivity to mechanical and thermal stimuli appear to be mutually exclusive. Materials with sufficiently large energy content are often too sensitive to find a practical use, and many energetic materials with adequate stability do not meet the performance requirements.

Nitrogen-rich compounds are new members of high-energy density materials, and they are environmentally acceptable, which relies on their highly efficient gas production and also on their high heat of formation for energy release, because nitrogen gas has a zero heat of formation and is the major product of decomposition [1–6]. Because of positive heat of formation and good thermal stability, nitrogen heterocyclic rings have received a great deal of interest as ligands to construct energetic coordination compounds [3,7–10]. T. M. Klapötke reported on the synthesis and characterization of a series of nitrogen-rich salts of 5,5-bistetrazolates, such as dihydroxylammonium (TKX-50), diammonium 5,5′-bistetrazole-1,1′-diolate (ABTOX) [11–14], while Rui Hu Wang on the synthesized of a series of nitrogen-rich salts of 5,5-bistetrazolates [15]. Magnesium metal energetic complexes have attracted considerable interest especially in primary explosives and energetic catalysts in pyrotechnic and propellant mixtures because of their potential properties, such as high energy, low sensitivities, and good catalytic performance [16–18]. In this paper, we reported the synthesis and structures of metal energetic complex Mg with 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] dihydrate (DNABT). Furthermore, thermal decomposition processes and sensitivity were explored.

Materials and instruments. All chemicals from commercial sources were of analytical purity and used without furification.

Infrared spectra were measured with a Bruker Spectrum One FT-IR spectrometer as KBr. ^{1}H NMR and ^{13}C NMR were recorded with a Bruker instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane. To measure elemental analysis, Vario EL III was employed. To determine the thermolysis performance of DNABT and target compounds, the SHIMADZU DTG–60 (heating rate 5 K/min) were used. The impact sensitivities of the mid-compound and melt

salts were determined with a fall hammer apparatus. At the time of the test, the room temperature was 23°C and relative humidity was 65%. A sample (30 mg) was placed between two steel poles and hit with a 5.0-Kg drop hammer from a starting height of 25 cm. The friction sensitivity of the melt salts was also measured with the MGY–1 pendular friction sensitivities apparatus according to the standard procedure with 20 mg of sample, when sample was compressed between two steel poles with mirror surfaces at a pressure of 3.92 Mpa and then hit with 5-Kg hammer at a 90° angle relative to the horizontal.

Crystallographic data collection and structure determination. The crystal of compound **1** was grown in methanol solution by slow evaporation at room temperature. A yellow crystal of **1**, irregularly shaped, of approximate dimensions 0.22 × 0.20 × 0.18 mm^3, was used for crystal and intensity data collection. The crystal of compound **4** was grown in water by slow evaporation at room temperature. A pale yellow crystal of **4**, irregularly shaped, of approximate dimensions 0.22 × 0.21 × 0.20 mm^3, was used for crystal and intensity data collection. The crystal of **1** and **4** was measured on a Bruker–AXS smart APEX2 CCD detector using a Mo–Kα radiation wavelength of λ = 0.71073 Å. The structures were measured at 296 K. The data collection and data reduction were carried out with the Saint Plus software. The crystal structure of **1** and **4** was solved by direct method with SHELXL 97 program and refined by full-matrix least squares on F2 with anisotropic displacement parameters for all non-H atoms.

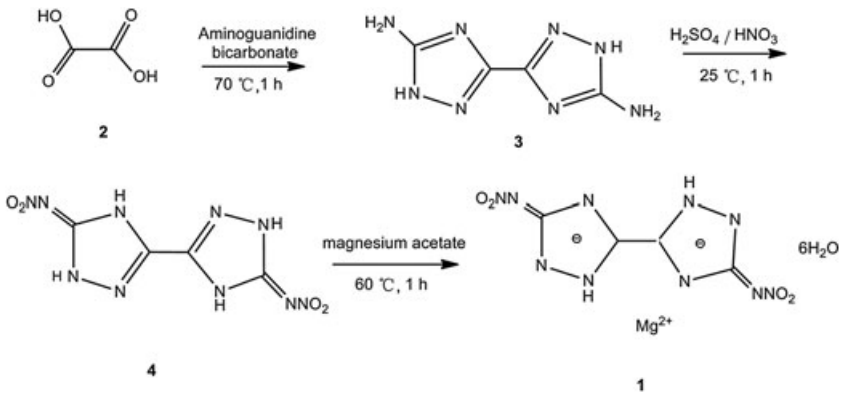
RESULTS AND DISCUSSION

Synthesis. Magnesium 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] hexahydrate was synthesized according to Scheme 1. DNABT bears two protons that are readily available in aqueous solution, and it can be deprotonated by reaction with the respective alkali metal hydroxides or carbonates. The choice of the metal source has to depend on the solubility of the material, and for the preparation of magnesium salt (**1**), magnesium acetate was used. The solubility of DNABT is fairly good in hot water, but poor in cold water. The reactions therefore were carried out under high temperature in water, but ensure that the starting material is fully dissolved.

Structural description of compounds 1 and **4**. Magnesium 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] hexahydrate (**1**) crystallizes in the Triclinic space group P-1(2) with one molecule in each unit cell. The density of **1** is 1.707 g/cm^3, and a unit cell volume is 376.0(2) $Å^3$; this can be attributed to the higher number of water molecules in the unit cell. Each cation is surrounded by six water molecules, with very little variation in the contact distances (2.0–2.1 Å), forming slightly distorted octahedrons.

In comparison with neutral DNABT, there are no significant changes regarding the bonds length (N1−N2 = 1.3016(40) Å, N2−C1 = 1.3856(37) Å, C1−N3 = 1.3423(28) Å, N3−N4 = 1.3648(40) Å, N4−C2 = 1.3235(39) Å, N5−C2 = 1.3656(31) Å, C2−C2 = 1.4749(52) Å). The bond angle in **1** N3−C1−N5 (109.632(230)°) and N4−C2−N5 (114.929(200)°) are larger than in neutral 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate], whereas the others angle are smaller than in the neutral 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate]. The five membered 6π electron aromatic triazolate rings are planar for $DNABT^{2-}$ (torsion angle N3−N4−C2−N5 = (−0.495°(318), N3−C1−N5−C2 = (−0.581°(308)), and the triazolate rings are almost planar for DNABT (torsion angle N3−N4−C2−N5 = (−0.899°(238), N3−C1−N5−C2 = (−0.744°(227)). The torsion angles of O2−N1−N2−C1 and O1−N1−N2−C1 of **1** are respectively −2.395° (404) and 177.081° (242), while

Scheme 1. Synthetic processes of **1**.



torsion angle of O2−N1−N2−C1 and O1−N1−N2−C1 of DNABT are respectively 1.878° (318) and 177.709 (196). Figure 1 shows the molecular structure of **1**, Fig. 2 shows the resulting layer structure of **1** along the *c* axis, and Fig. 3 shows the resulting pack structure of **1**. The packing of **1** can be described as a vertical layer structure along the *b* axis, with alternating alignments of octahedrally coordinated Mg^{2+}cations as well as the DNABT anions. Table 1 shows the results of the crystal structure solution and refinement for compounds **1** and **4**.

Thermal decomposition. Under the linear heating rate of 5 K/min, TDA-TG experiments were carried out in order to investigate the thermal behaviors of **4** and **1**. The TDA-TG curves are illustrated in Fig. 4.

The TDA-TG curves for **4** show one endothermic peak and one exothermic peak, one sharp for the endothermic process at 108°C with the loss of one water molecules and the other broad for the decomposition process at 201°C. In endothermic process, the observed mass loss value is 13.4%, and in exothermic process the mass loss value is 64.7%.

The TDA-TG curves for the thermal decomposition of **1** show one endothermic peak and one exothermic peak. TG curves showed that the thermal decomposition of **1** can be divided into two principal stages, the first stage occurs in

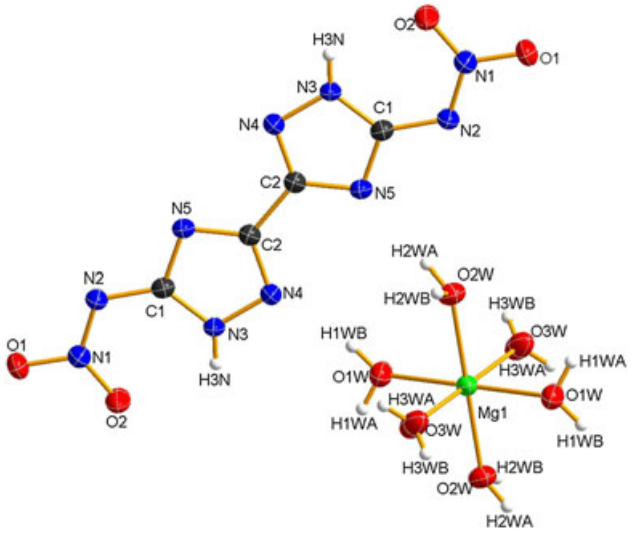


Figure 1. Molecular structure of magnesium 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] hexahydrate (**1**). [Color figure can be viewed at wileyonlinelibrary.com.]

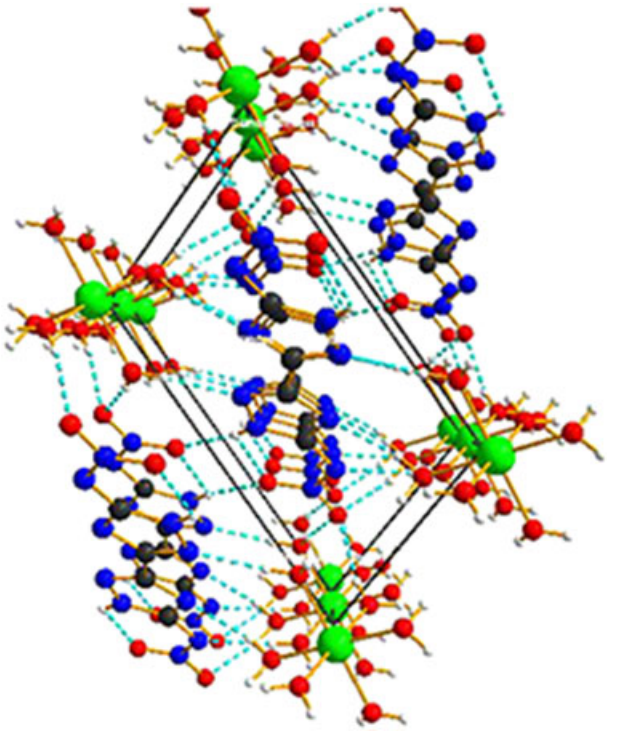


Figure 3. Crystal packing structure of complex magnesium 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] hexahydrate (**1**). [Color figure can be viewed at wileyonlinelibrary.com.]

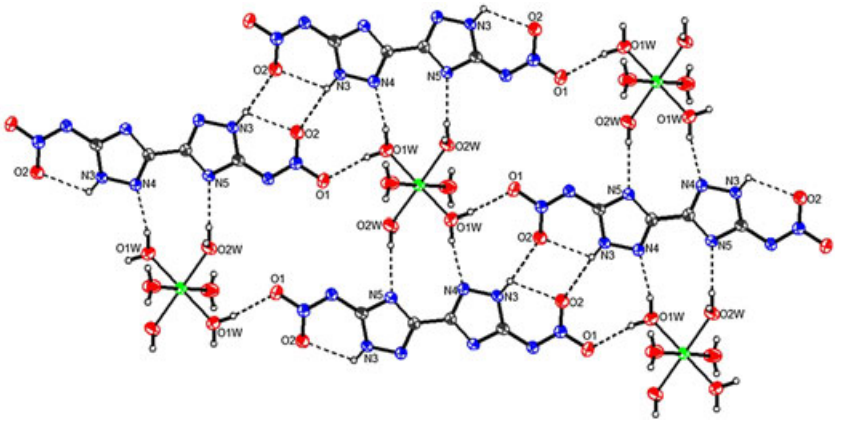


Figure 2. Extended structure of magnesium 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] hexahydrate (**1**). [Color figure can be viewed at wileyonlinelibrary.com.]

Table 1

Crystallographic data and structure refinement details for compounds **1** and **4**.

Compound	**4**	**1**
Chemical formula	$C_4H_8N_{10}O_6$	$C_4H_{22}N_{10}O_{10}Mg$
Formula weight/g •mol^{-1}	292	394.56
Crystal size / mm	0.22 × 0.21 × 0.20	0.22 × 0.20 × 0.18
Crystal system	Monoclinic	Triclinic
Crystal group	P21/n	P-1(2)
a / Å	5.223(6)	5.873(19)
b / Å	17.83(2)	6.746(2)
c / Å	6.308(7)	10.717(4)
α /°	90	72.202(5)
β /°	112.48(2)	87.260(7)
γ /°	90	68.808(5)
v /Å^3	542.8(11)	376.0(2)
z	2	1
$\rho_{calc.}$ / g•cm^{-3}	1.788	1.707
μ mm^{-1}	0.163	0.197
F(000)	300	200
θ range/°	2.28~25.19	2~25.47
Refl. collected	3224	2117
Refl. unique	840	1061
R (int)	0.025	0.0618
Data / rest. / param	970 / 2 / 99	1371 / 9 / 137
GOOF	1.052	1.035
R_1, wR_2 [$I > 2\sigma(I)$]	0.0589, 0.1552	0.0453, 0.1213
R_1, wR_2(all data)	0.0541, 0.1462	0.0618, 0.1342
CCDC numbers	1056722	1421776

the range of 74–180°C with the loss of six water molecules, in the DTA cures of **1**, The exothermic decomposition was recorded in the second stage in the temperature range of 200–240°C. The magnesium salt shows a decomposition temperatures that are higher than neutral DNABT.

Sensitivity test. In order to study the stability and the hazardous nature of the complexes, the sensitivity properties of the ligand DNABT and **1** were tested. The sensitivity test results show that DNABT and magnesium complex is insensitive energetic compounds.

The friction sensitivity was measured by applying MGY-1 pendular friction sensitivities apparatus. The friction sensitivity of **4** is 36%, and the complex of magnesium is 12%, which is lower than that of RDX (48%).

To test the impact sensitivity, 30-mg sample was placed between two steel poles and hit with 5.0-Kg drop hammer from a starting height of 25 cm. The results of the impact sensitivity test showed that the P% of **4** and **1** all are 48% and 0%.

Combustion behavior. Initially, the combustion behavior of the compounds **1** was qualitatively characterized with a simple smoke test method. Approximately 1-g sample was placed in a heated crucible with a gas torch for observation of color, smoke, burn ability, and level of residue. Results are summarized in Table 2.

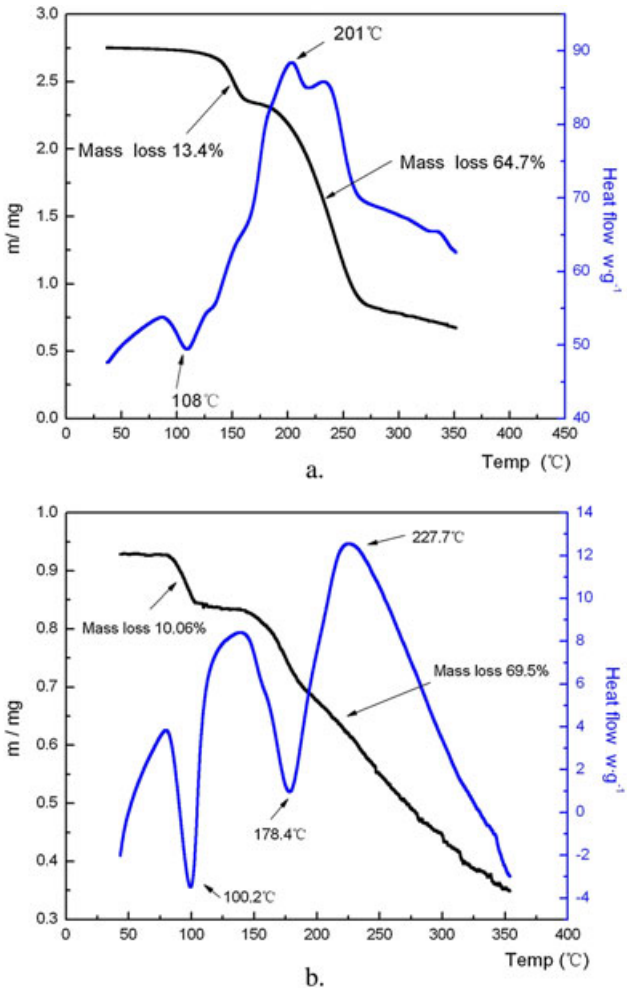


Figure 4. DTA-TG cures of **4** (a) and **1** (b). [Color figure can be viewed at wileyonlinelibrary.com.]

Table 2

Combustion behavior summary of compounds **1**.

Compound	Color	Smoke	Burn ability	Residue
1	White	No	No	Yes

The results suggest that compound **1** produces desirable white flames and nearly smokeless, after the combustion **1** left solid residues. This makes especially **1** as promising candidates for white colorants in modern smokeless pyrotechnical compositions.

CONCLUSIONS

Alkaline Earth metal magnesium energetic complex **1** has been synthesized and well characterized by IR spectroscope, elemental analysis, and single-crystal X-ray diffraction. The crystal of compound **1** was found as

triclinic space group P-1(2) with 1 molecular in the unit cell. The thermal stabilities were analyzed by differential thermal gravity/thermal gravity analysis, the complex of magnesium is more stable than neutral DNABT, and the complex **1** has high decomposition temperature of 227°C. The sensitivities were determined against impact and friction. The complex turned out to insensitive toward impact (P = 0%) and friction (P = 12%). The complex **1** has good color performance and combustion behavior.

EXPERIMENTAL

Caution. DNABT and its coordination compound are energetic materials with increased sensitivities toward shock and friction. Therefore, proper safer precautions (safety glass, face shield, earthed equipment, shoes, gloves, and ear plugs) have to be applied when synthesizing and handling the described compounds.

Synthesis of 5,5′-diamino-3,3′-bis(1*H*-1,2,4-triazole) (3). Hydrochloric acid (60 mL) was added to a stirred mixture of oxalic acid (20.0 g, 159 mmol) and aminoguanidinium bicarbonate (45.4 g, 332 mmol). The reaction was stirred at 70°C for 1 h, and the precipitate was collected by filtration. The colorless solid was dissolved in water (240 mL) and alkalized with sodium hydroxide to pH = 14. The resulting precipitate was collected by filtration, washed with water (~200 mL), and dried in air to yield 3,3′-diamino-5,5′-bis(1H-1,2,4-triazole) (18.6 g, 112 mmol, 70%) as a colorless solid.

IR: ν(cm^{-1}) = 3325(m), 3116(m), 2863(m), 2784(m), 1706(m), 1668(s), 1654(s), 1618(m), 1606(m), 1484(m), 1457(m), 1267(m), 1104(vs), 1061(s), 987(w), 956(w), 721(s). ^{1}H NMR (300 MHz, DMSO-d_6, 25°C, ppm): =6.48 ppm (s, 2H, NH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 25°C, ppm): =157.7, 149.1 ppm. Elemental analysis ($C_4H_6N_8$): calcd. C 28.92, H 3.62, N 67.46; found: C 28.73, H, 3.59, N 67.88.

Synthesis of 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] dihydrate (4). Nitric acid (98%, 3.0 mL) was added slowly to a solution of 5,5′-diamino-3,3′-bis(1*H*-1,2,4-triazole) (1.0 g, 6.0 mmol) in concentrated sulfuric acid (9.0 mL) at 0°C. The mixture was allowed to warm to room temperature and stirred for 1 h. The solution was poured on ice, and the precipitate was collected by filtration and recrystallized from boiling water to yield 5,5′-dinitrimino-3,3′-bis(1H-1,2,4-triazole) dihydrate (1.35 g, 4.6 mmol, 77%) as yellow crystalline solid.

IR: ν(cm^{-1}) = 3165(m), 3154(m), 1706(m), 1565(vs), 1508(s), 1446(s), 1380(m), 1298(vs), 1229(vs), 1140(m), 1085(m), 1054(s), 989(m), 947(s), 849(m), 778(s), 766(s), 751(s). ^{1}H NMR (300 MHz, DMSO-d_6, 25°C, ppm): = 5.51 ppm (s, 2H, Triazole. ^{13}C NMR (75 MHz, DMSO-d_6, 25°C, ppm): = 153.2, 143.6 ppm. Elemental analysis ($C_4H_8N_{10}O_6$): calcd. C 16.44, H 2.74, N 47.95; found: C 16.61, H, 2.68, N 47.58.

Synthesis of magnesium 5,5′-dinitramino-3,3′-bi[1,2,4-triazolate] hexahydrate [Mg(DNABT)(H_2O)$_6$] (1). 5,5′-Dinitrimino-3,3′-bis(1*H*-1,2,4-triazole) dihydrate (2.92 g, 10 mmol) was dissolved in distilled water (60 mL). A solution of magnesium acetate (3.21 g, 15 mmol) in water (30 mL) was added, and the suspension was stirred for 60 min at 60°C, then cooled down and filtered. The obtained solid was washed with water then dried in air to a yellow solid (2.6 g, 66%).

IR: ν(cm^{-1}) = 3191(m), 3152(m), 1566(vs), 1510(s), 1445(s), 1381(m), 1229(vs), 1138(m), 1088(m), 1055(s), 989(m), 949(s), 849(m), 768(s), 755(s). Elemental analysis ($C_4H_{22}N_{10}O_{10}Mg$): calcd. C 12.17, H 5.58, N 35.48; found: C 12.32, H, 5.49, N 35.15.

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