



Synthesis, characterization and properties of a new energetic salt 2,4-diamino-6-methyl-1,3,5-triazine dinitramide



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ABSTRACT

A new nitrogen-rich energetic salt, 2,4-diamino-6-methyl-1,3,5-triazine dinitramide, was synthesized by combining silver dinitramide and 2,4-diamino-6-methyl-1,3,5-triazine perchlorate. The structure of this new energetic salt was confirmed using single-crystal X-ray diffraction, elemental analysis, Fourier transform infrared spectrometry, ultraviolet–visible spectrophotometry, and nuclear magnetic resonance spectroscopy. The thermal stability was determined using differential scanning calorimetry, differential thermal analysis, and thermogravimetric tandem infrared spectrometry. Results showed that the target compound exhibits good thermal decomposition resistance of up to 470 K and has 59.1% mass loss with $E_a = 118.2 \text{ kJ mol}^{-1}$. Additionally, the detonation pressure and velocity obtained using Kamlet-Jacobs equations are 23 GPa and 8.2 km s^{-1} , respectively. Sensitivity test was also attempted. The impact sensitivity of this new energetic salt is 11.5 J, which is superior to that of RDX (7.4 J).

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1. Introduction

As a significant branch of materials science, energetic materials including explosives, pyrotechnics and propellants, are widely investigated for military and civilian applications [1–4]. High-energy density materials (HEDMs), wherein energetic nitrogen-rich salts are among the recent developments, continue to attract considerable attention. Energetic nitrogen-rich compounds are potential and promising candidates for HEDMs because of their high heat of formation and high density due to their large number of energetic N–N and C–N bonds [5–9]. Moreover, salt-based energetic materials are often better than non-ionic molecules because of their lower vapor pressures and higher densities.

Synthesis of energetic salts involves combining unique cations and anions possessing energetic functionalities. Five- or six-membered nitrogen-rich heterocyclic compounds, such as triazole, tetrazole, triazine and tetrazine have been utilized in energetic roles owing to their high heat of formation, density and oxygen balance compared with those of their carbocyclic analogues [10].

Most frequently anion such as nitrate, perchlorate and dinitramide, are inorganic.

Preparation of many new organic energetic salts of dinitramide requires appropriate dinimide transfer reagents [11]. However, free dinitramine is not promising because of its instability, and decomposing at 273.15 K [12]. Silver dinitramide ($\text{AgN}(\text{NO}_2)_2$) is an excellent dinitramide transfer reagents [11]. Moreover, 1,3,5-triazine rings (or s-triazine), which have been studied for use in numerous applications, such as herbicides, synthesis, dyes, and polymers [13–16] due to their positive heat of formation and stability, are promising candidates for combining with the dinitramide anion, $\text{N}(\text{NO}_2)_2^-$ (DN). Herein, a simple synthesis of a new high-nitrogen dinitramide salt compound based on triazine cation rings and $\text{AgN}(\text{NO}_2)_2$ is presented. The molecular structure and thermodynamics were analyzed to verify its purity, high energy and insensitive properties.

2. Results and discussion

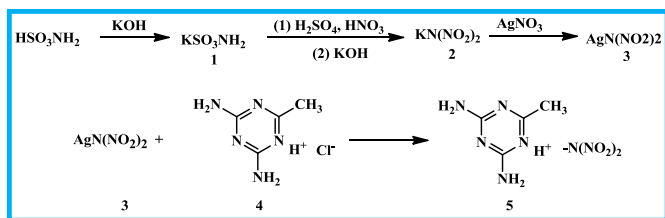
2.1. Syntheses

Silver dinitramide ($\text{AgN}(\text{NO}_2)_2$) was prepared by a modified procedure according to a previous procedure [11,17]. $\text{AgN}(\text{NO}_2)_2$ was synthesized starting from sulfamic acid (HSO_3NH_2), which was

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Scheme 1. The synthesis of 2,4-diamino-6-methyl-1,3,5-triazine dinitramide.

treated with potassium hydroxide (KOH) to form compound **1**. Compound **1** was then nitrated and reacted with KOH to obtain **2**. The cation exchange reaction between **2** and silver nitrate resulted in compound **3**, $\text{AgN}(\text{NO}_2)_2$. Compound **4** was obtained through acidification process. Target product **5**, 2,4-diamino-6-methyl-1,3,5-triazine dinitramide, was formed through anion exchange between **3** and **4**, as shown in [Scheme 1](#).

2.2. Spectroscopy

The structures of these prepared energetic compounds are supported by their corresponding FT-IR, UV–Vis, ^1H NMR, ^{13}C NMR, and elemental analysis. The data are listed in the Experimental Section. In the UV–Vis spectra ([Fig. 1](#)), the compound **5** exhibited strong absorption in the region of 260–320 nm, with a maximum absorption at 284 nm, corresponding to the dinitramide anion [12]. In the IR spectra ([Fig. 2](#)), strong absorption peaks at 1529 and 1384 cm^{-1} were ascribed to the stretching vibration and asymmetrical stretching vibration of $-\text{NO}_2$, similar to other dinitramide salts [18]. The peak at 1693 cm^{-1} corresponded to the typical stretching modes of $\text{C}=\text{N}$. The main characteristic peak at 1191 cm^{-1} was attributed to the $\text{C}-\text{N}$ stretching vibration absorption. Three peaks around 3151 cm^{-1} were related to the stretching vibration of $\text{C}-\text{H}$ at the triazine. The broad band around 3398 cm^{-1} was designated to the amine. The ^1H NMR and ^{13}C NMR spectra ([Fig. 3](#)) have also confirmed the correct structure of **5**. In the ^1H NMR [DMSO- d_6] spectrum, the amino group protons of salt appeared at $\delta = 7.10$ ppm (t, 4 H, NH_2) and the methyl group appeared at $\delta = 2.30$ ppm (s, 3 H, CH_3). In the ^{13}C NMR [DMSO- d_6] spectrum, the methyl group signals were found at $\delta = 21.50$ ppm and the triazine ring appeared at $\delta = 166.87$ ppm.

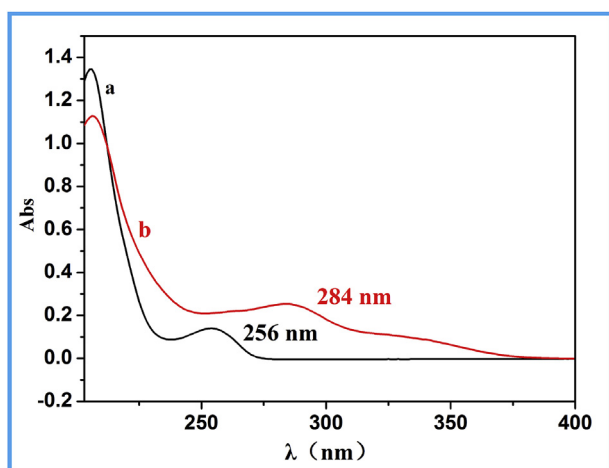


Fig. 1. UV–Vis spectra of compound **5**.

2.3. Crystal structures

Crystals of **5** that were suitable for single-crystal X-ray diffraction were cultured by slowly evaporating ethanol at room temperature and normal pressure. The selected crystallographic data are summarized in [Table 1](#). And further information about crystal-structure determinations is given in the [ESI](#). Compound **5** crystallizes in the monoclinic space group P-1 with a calculated density of 1.678 g cm^{-3} , based on the two molecules packed in the unit-cell volume of 459.47 (13). In [Fig. 4a](#), the molecular unit of crystalline **5** consists of one dinitramide anion and one crystallographically independent cation. For the anion, a small torsion angle at N (6)–N (7)–N (8)–O (3) of -10.86 (16)° was detected ([Table S1](#)). As seen in [Table S2](#), the bond lengths of N (6)–N (7) [1.3742 (14) Å] and N (7)–N (8) [1.3809 (14) Å] are between the lengths of N–N single (1.454 Å) and N=N double (1.245 Å) bonds [19]. The C–N bond lengths in the s-triazine ring vary from 1.3171(14)–1.3795(14) Å, which are between the lengths of C–N single (1.470 Å) and C=N double (1.220 Å) bonds [19,20]. Moreover, the bond angles of nitrogen heterocyclic within $115.35(10)$ – $125.23(10)$ ° are close to 120° , which further confirms the tautomerism of s-triazine rings. Among the bonds in the crystal of **5**, two kinds of hydrogen bonds exist: one is the hydrogen bonds between anions and cations, and the other is between cations and cations. Its packing structure is configured by hydrogen bonds; the extensive hydrogen-bonding interactions form a complex 3D network ([Fig. 4b](#)). Further details are provided in [Table S3](#).

2.4. Thermal behavior

Thermal stability is crucial for energetic materials and unsatisfactory thermal stability limits applications [21]. Compound **5** was examined through DSC and TGA at a heating rate of 10 K min^{-1} . In [Fig. 5](#), the maximum decomposition temperature is at 470 K, and the corresponding enthalpy is 1854 J g^{-1} . The salt **5** undergoes only one mass loss stage ([Fig. 6](#)), corresponding to the peak in the DSC curve. A rapid weight loss was observed at 468 K, accompanied by approximately 59.1% mass loss; it may be attributed to the simultaneous decomposition of s-triazine rings and dinitramide anions.

To understand the thermal decomposition behavior of compound **5**, a thermogravimetric analysis with an infrared spectrum was investigated. [Fig. 7](#) shows the IR spectra of the thermal decomposition gas at different decomposing temperatures. The

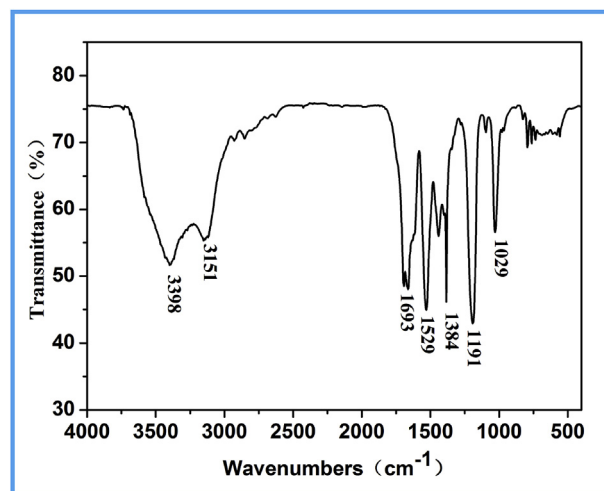


Fig. 2. FT-IR spectra of compound **5**.

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