



## Synthesis and characterization of energetic salts based on the new propan-2-ylidene methanetriamium cations



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### HIGHLIGHTS

- Propan-2-ylidene methanetriamium is the new structures.
- Bond homogenization of the salts suggests delocalization of the charge.
- The salts are hypergolic with white fuming nitric acid.

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### ABSTRACT

Development of new hypergolic ionic liquids is the key in replacing toxic N,N-dimethylhydrazine as green liquids propellants. Three salts based on the new propan-2-ylidene methanetriamium cations and dicyanamide anion were synthesized and characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR and Raman spectroscopy, elemental analysis, and TG/DTA. In addition, their crystal structures were determined by X-ray single crystal diffraction. N-(propan-2-ylidene) methanetriamium dicyanamide (**1**) crystallizes in the monoclinic space group *P2<sub>1</sub>/n*, N,N'-bi(propan-2-ylidene) methanetriamium dicyanamide (**2**) in triclinic *P-1*, and N,N',N''-tri(propan-2-ylidene) methanetriamium dicyanamide (**3**) in monoclinic *C2/c*. With heats of formation (from 1.56 to 1.80 kJ g<sup>-1</sup>) and densities (from 1.19 to 1.31 g cm<sup>-3</sup>) in hand, the detonation pressure (*P*) and velocity (*D*), and specific impulse (*I<sub>sp</sub>*) values of salts were calculated as 8.94 GPa, 4989 m s<sup>-1</sup> and 174.3 s (**1**), 7.91 GPa, 4815 m s<sup>-1</sup> and 179.0 s (**2**), and 7.33 GPa, 4693 m s<sup>-1</sup> and 180.6 s (**3**), respectively. Impact sensitivities of **1**, **2** and **3** were measured to be no less than 40 J by hammer tests, which places these salts in the insensitive class. Moreover, the resulting salts are hypergolic with white fuming nitric acid and exhibit potential as bipropellants.

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### Introduction

During the development of high-density energetic materials, energetic ionic liquids (salts) with lower vapor pressure and better thermal stability than their atomically similar nonionic analogues, have attracted considerable interest [1–6]. Interestingly, ionic liquids with the dicyanamide anion (N(CN)<sub>2</sub><sup>-</sup>) were hypergolic with oxidizers (HNO<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>), and become the potential replacement of N,N-dimethylhydrazine as liquid propellants [7–12]. Though

the key to the hypergolicity of ionic liquids was the anions, such as <sup>-</sup>N(CN)<sub>2</sub>, <sup>-</sup>N(CN)(NO<sub>2</sub>), and <sup>-</sup>BH<sub>2</sub>(CN)<sub>2</sub>, Zhang et al. found that cations also play an important role in modifying the properties of ionic liquids, including density, viscosity, thermal stability, and ignition delay time [7]. Compared with the alkyl-substituted imidazolium, pyridinium, and pyrrolidinium [11], guanidinium with higher nitrogen content and heat of formation is the common cations of energetic salts. In addition, guanidinium salts exhibit strong hydrogen bonding networks, which contributes to good thermal stability and low impact sensitivity [13]. The previous studies have given strong supports that the guanidinium unit is an excellent candidate for a new generation of energetic salts, which provided the opportunity to obtain the desired properties by tuning cation structures [14,15]. However, whether guanidinium cations may

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contribute to the hypergolicity of energetic salts has not been investigated.

In this paper, 3 energetic salts were obtained with the new propan-2-ylidene methanetriamium cations and dicyanamide anion. They were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR and Raman spectroscopy, and elemental analysis. The structures of the salts were determined by X-ray single-crystal diffraction. Their thermal behavior was studied using TG/DTA. Properties such as heats of formation, densities, detonation performances, and impact sensitivities were studied by theoretical and experimental methods. The hypergolic properties of the salts were also examined with white fuming nitric acid (WFNA) as oxidizer.

## Experimental

### Materials and methods

All reagents and solvents were obtained commercially as analytical grade, and employed as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded on a Bruker 600 MHz spectrometer, with  $[\text{D}_6]$  DMSO as the locking solvent. The chemical shifts were given in ppm relative to tetramethylsilane (TMS). Infrared (IR) spectra were recorded on a Thermo Nicolet 380 spectrometer using KBr pellets at room temperature. The Raman spectra were recorded on a Bruker RFS100/S at 514 nm. Elemental analysis (C, H, N) was performed with a Vario EL elemental analyzer. Densities were measured at room temperature on a Micromeritics Accupyc 1340 gas pycnometer. Thermogravimetric (TG/DTA) measurements were performed at different heating rates (2, 5, 10, and  $15\text{ }^\circ\text{C min}^{-1}$ ) with a nitrogen flow of  $80\text{ ml min}^{-1}$  in Al-container. The kinetic parameters were obtained by Kissinger and Ozawa methods.

### X-ray crystallography

The crystal structure analysis was performed on a Bruker CCD X-ray diffractometer equipped with an area detector, and the crystals were irradiated using graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.7103\text{ \AA}$ ). Data collection was performed and the unit cell was initially refined using APEX2 [16]. Data reduction was performed using SAINT [17] and XPREP [18]. Absorption corrections were applied using SADABS [19]. The structure was solved and refined with the aid of the SHELXTL software package

[20]. The full-matrix least-squares refinement on  $F^2$  included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included using a riding model.

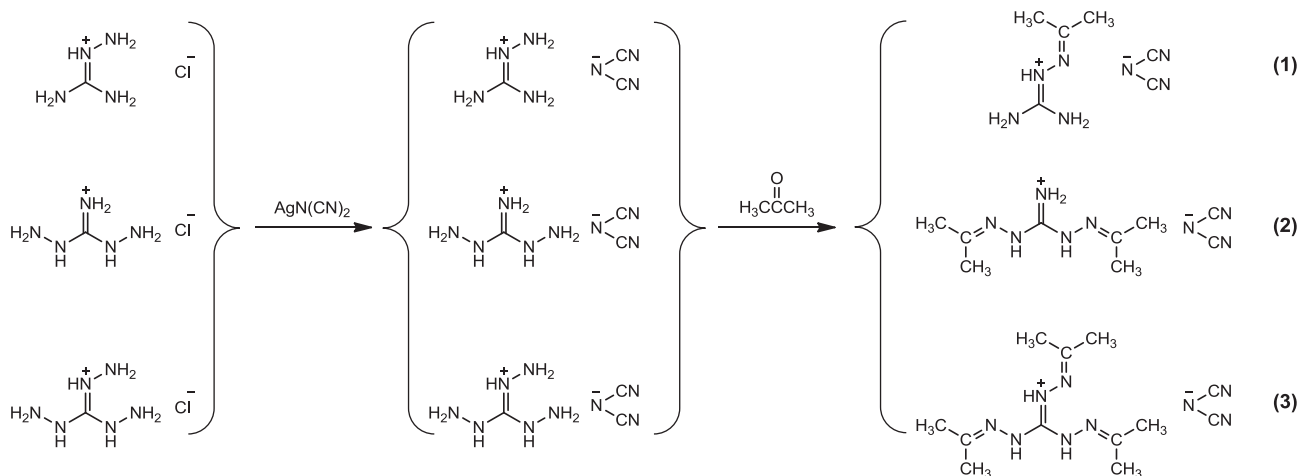
### Synthesis of 1, 2, and 3

N-(propan-2-ylidene) methanetriamium dicyanamide (1), N,N'-bi(propan-2-ylidene) methanetriamium dicyanamide (2), and N,N',N''-tri(propan-2-ylidene) methanetriamium dicyanamide (3) were readily synthesized by reacting acetone with the corresponding guanidinium-based dicyanamide which were obtained by the metathetical reactions of silver dicyanamide with aminoguanidinium, diaminoguanidinium, and triaminoguanidinium hydrochloride in water (or methanol), respectively (Scheme 1).

**Silver dicyanamide:** A solution of sodium dicyanamide (2.56 g, 28.8 mmol) in water (50 ml) was added to a stirring solution of silver nitrate (4.89 g, 28.8 mmol) in water (50 ml). The precipitate was filtered and washed with a small amount of water. After dried, a white solid was obtained in high yield (4.75 g, 95%).

**N-(propan-2-ylidene) methanetriamium dicyanamide (1):** The aqueous solution of aminoguanidinium hydrochloride (2.21 g, 20 mmol) in 20 ml  $\text{H}_2\text{O}$  was added dropwise into the suspension of silver dicyanamide (4.18 g, 24 mmol) in 30 ml  $\text{H}_2\text{O}$ . After stirring at room temperature overnight, the insoluble silver chloride and excess silver dicyanamide were removed by filtration. The resulting solution was evaporated under reduced pressure to give aminoguanidinium dicyanamide. The crude aminoguanidinium dicyanamide was dissolved in 30 ml acetone, and stirred for 30 min. After filtration, the acetone solution was vaporized slowly in room temperature to yield colorless crystals (2.77 g, 76%).  $^1\text{H}$  NMR ( $\text{D}_6$ -DMSO):  $\delta = 10.05$  (s, 1H; NH), 7.30 (s, 4H;  $\text{NH}_2$ ), 1.95 ppm (s, 6H;  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{D}_6$ -DMSO):  $\delta = 155.9, 120.0, 25.3, 18.0$  ppm. IR (KBr):  $\nu = 3391, 3305, 3150, 3040, 2251, 2213, 2147, 1671, 1623, 1540, 1364, 1319, 1275, 1139, 620, 597, 518, 500, 467\text{ cm}^{-1}$ . Raman (514 nm): 2927, 2209, 2144,  $1655\text{ cm}^{-1}$ . Anal. Calc. (%) for  $\text{C}_6\text{H}_{11}\text{N}_7$  (181.20): C, 39.77; H, 6.12; N, 54.11; Found: C, 40.12; H, 6.02; N, 54.45.

**N,N'-bi(propan-2-ylidene) methanetriamium dicyanamide (2):** The same procedure was followed as used for 1. Diaminoguanidini-



Scheme 1. Synthesis of 1, 2, and 3.

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