Green primaries: Environmentally friendly energetic complexes

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Primary explosives are used in small quantities to generate a detonation wave when subjected to a flame, heat, impact, electric spark, or friction. Detonation of the primary explosive initiates the secondary booster or main-charge explosive or propellant. Long-term use of lead azide and lead styphnate as primary explosives has resulted in lead contamination at artillery and firing ranges and become a major health hazard and environmental problem for both military and civilian personnel. Devices using lead primary explosives are manufactured by the tens of millions every year in the United States from primers for bullets to detonators for mining. Although substantial synthetic efforts have long been focused on the search for greener primary explosives, this unresolved problem has become a ''holy grail'' of energetic materials research. Existing candidates suffer from instability or excessive sensitivity, or they possess toxic metals or perchlorate. We report here four previously undescribed green primary explosives based on complex metal dianions and environmentally benign cations, $(cat)_2[M^{II}(NT)_4(H_2O)_2]$ (where cat is NH_4^+ or Na^+, M is Fe^{2+} or Cu^{2+}, and NT^- is 5-nitrotetrazolato-N^2). They are safer to prepare, handle, and transport than lead compounds, have comparable initiation efficiencies to lead azide, and offer rapid reliable detonation comparable with lead styphnate. Remarkably, they possess all current requirements for green primary explosives and are suitable to replace lead primary explosives in detonators. More importantly, they can be synthesized more safely, do not pose health risks to personnel, and cause much less pollution to the environment.

copper | green | iron | primary explosives | tetrazole

In the early 1900s, lead azide (LA) (1) and lead styphnate (LS) (2) were identified as the only viable primary explosives to replace mercury fulminate (3, 4). Their use as replacements was motivated by the desire to eliminate mercury toxicity and improve explosive performance including shelf life. Multicomponent compositions of lead primary explosives with improved performance have been developed for specialized applications in military and civilian ammunition, but long-term environmental contamination, health effects, and hazards from extreme sensitivities have made their replacement essential (5).

The U.S. Army alone consumes >1,000 pounds of lead primary explosives per year with 710 pounds of that lead. A 1991 survey showed that employees working at an FBI shooting range in Quantico, VA, had in-cell blood lead levels nearly 10 times higher than the limits set by the U.S. government (6). In 1993, President Clinton issued a series of executive orders (No. 12866) to reduce or eliminate procurement of hazardous substances and chemicals by federal facilities (7). Identification of suitable lead replacements for LA is very challenging because replacement candidates must have explosive performance comparable with LA and instantaneous response to detonation comparable with LS and yet meet acceptable health and safety standards.

Lead replacements must retain energetic properties upon exposure to the atmosphere and must have the following qualities: (*i*) insensitivity to light; (*ii*) sensitivity to detonation but not too sensitive to handle and transport; (*iii*) thermally stable to at least 200°C, (*iv*) chemically stable for extended periods; (*v*) devoid of toxic metals such as lead, mercury, silver, barium, or antimony; and (*vi*) free of perchlorate, which may be a possible teratogen and has adverse effects on thyroid function (refs. 8 and 9; see also ref. 10 and references therein).

Existing primary explosives include organic compounds, metastable innerstitial composites, and coordination complexes. Tetracene or 1-(5-tetrazolyl)-4-guanyltetrazene hydrate (TGTH) (Fig. 1) is degraded by boiling water (11), whereas diazodinitrophenol or 2-diazo-4,6-dinitrobenzene-1-oxide (DADNP) is darkened rapidly by exposure to sunlight (ref. 12, pp. 443–446). 1,3,5-triazido-2,4,6-trinitrobenzene (TATNB) is unstable to sunlight and undergoes nitrogen elimination followed by intramolecular rearrangement to become the secondary explosive benzotrifurozan (BTF) (ref. 12, pp. 436–438). Although 3,6-diazido-1,2,4,5-tetrazine (DiAT) (13) and 1,3,5-triazido-2,4,6-triazine (TAT) (14) are very powerful primary explosives owing to their high-energy azido groups, they are notorious for their poor thermal stability and extreme sensitivity to accidental initiation by impact, spark, and friction. Besides containing perchlorate, high-nitrogen 3,6-di(guanidinium)-1,2,4,5-tetrazine-1,4-di-*N*-oxide diperchlorate (DGTOP) does not have outstanding thermal stability and is tedious to prepare (15). Mixtures of aluminum nanoparticles and heavy metal oxides (metastable innerstitial composites) (16–18) are known to have appropriate sensitivity. However, instability toward atmospheric oxygen and moisture, safety concerns during large-scale production, and residual heavy metal contaminations have prevented their adoption as lead salt replacements. The thermally stable coordination complexes, penta(ammine)(5-cyanotetrazolate-N^2)cobalt(III) perchlorate (CP) (ref. 19 and references therein) and tetra(ammine)di(5-nitrotetrazolate-N^2)cobalt(III) perchlorate (BNCP) (ref. 20 and references therein) have desirable properties, but their perchlorate content makes them unacceptable.

A systematic assessment of existing primary explosives clearly reveals limitations for organic compounds from inadequate thermal stability to decomposition upon exposure to heat or light. Metastable innerstitial composites are undesirable because of air oxidation of nanoaluminum particles, and existing coordination complexes are disadvantaged by their anionic perchlorate partners.

Based on this analysis, we have concluded that a coordination complex anion or anions charge compensated by environmentally benign cations such as NH_4^+ or Na^+ would make ideal primary explosives (21).

Results

In general, the performance of an explosive is measured by its detonation velocity (V_D = 0–10 km/sec) and detonation

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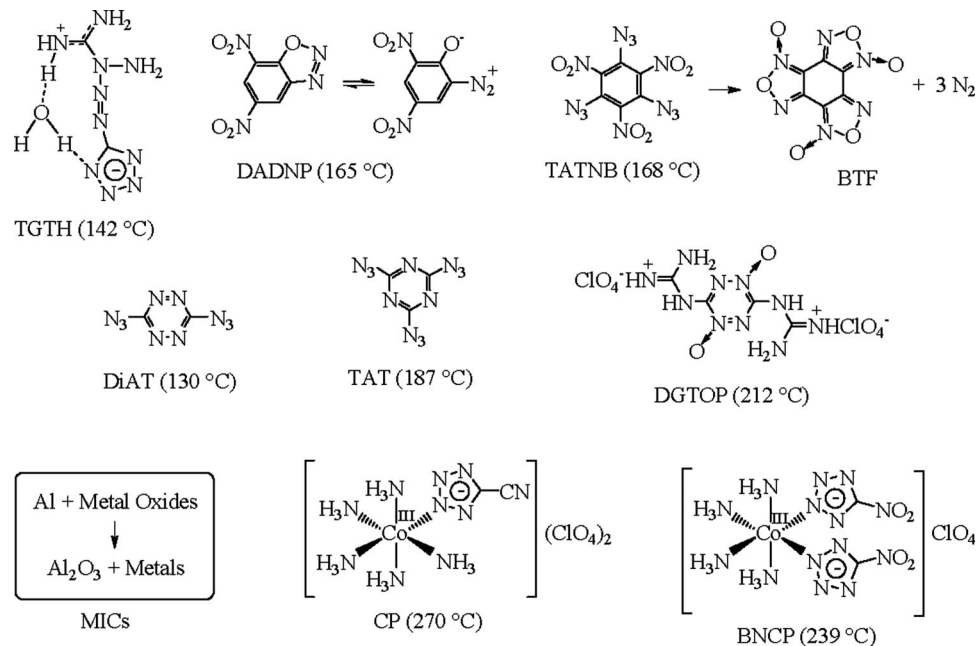
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Fig. 1. Representative examples of known primary explosives.

pressure (P_{CJ} = 0–420 kbar) which are determined by oxygen balance (OB_{CO}), heat of formation [ΔH_f (kJ/mol)], and density [ρ (g/cm^3)], e.g., the more positive oxygen balance, the higher positive heat of formation, and the higher the density, the better the performance. To achieve high explosive performance with a coordination complex, coordinated ligands must be highly energetic and rich in oxygen and nitrogen content, e.g., 5-nitrotetrazolato-N^2 (22). The extraordinary primary explosives reported here, (cat)$_2$[M^{II}(NT)$_4$(H$_2$O)$_2$] (catMNT), are synthesized in a nontoxic aqueous process. They are unique in containing four 5-nitrotetrazolato-N^2 ligands coordinated to the same metal center [Fe(II) or Cu(II)] and possess high positive OB_{CO}, even without perchlorate. More importantly, they meet all seven current desired criteria for green primary explosives (see Table 1).

Discussion

As shown in Table 1, replacement of the fuel-rich NH$_4^+$ cation by Na$^+$ dramatically enriches OB_{CO} (0.00 → 5.39) and explosive performance, as well as enhancing the friction sensitivity of (Na)$_2$[M^{II}(NT)$_4$(H$_2$O)$_2$] (NaMNT) (2,800 g → 20 g). The differences in crystal sizes in Fig. 2A reveal that friction sensitivity for (Na)$_2$[Fe^{II}(NT)$_4$(H$_2$O)$_2$] (NaFeNT) and (Na)$_2$[Cu^{II}(NT)$_4$(H$_2$O)$_2$] (NaCuNT) are enhanced by 140 and 12.5 times compared with their ammonium analogs, respec-

tively. Shown in Fig. 2B are the lid and sample holder from a differential scanning calorimetry experiment in which 0.75 mg of (NH$_4$)$_2$[Fe^{II}(NT)$_4$(H$_2$O)$_2$] (NH$_4$FeNT) was detonated at a scan rate of 5°C/min. In Fig. 2C *Left* and *Right* are the resulting aluminum blasting caps after 25 mg of NH$_4$FeNT and (NH$_4$)$_2$[Cu^{II}(NT)$_4$(H$_2$O)$_2$] (NH$_4$CuNT) were initiated by an electric match, respectively.

All primary explosives in Table 1 have excellent thermal stabilities, ≫200°C. The (Cat)$_2$[M^{II}(NT)$_4$(H$_2$O)$_2$] salts have similar impact sensitivities to LS. Notably, the detonation velocities of NH$_4$MNT are 30% higher than those of LA and LS even though their densities are much lower, V_D = 7.7 and 7.4 km/sec vs. 5.5 and 5.2 km/sec. The inverse proportionality between detonation velocity and density in this case is primarily due to the high density of energetically inert lead metal. LA and NH$_4$MNT have zero OB_{CO}, whereas LS and NaMNT have comparable high positive OB_{CO} values, 5.33 vs. 5.39 and 5.32).

The NH$_4$MNT salts have the least friction sensitivity. NaMNT and LS have comparable friction sensitivities, but they are three times less sensitive than LA. Unlike the spark insensitivity of (Cat)$_2$[M^{II}(NT)$_4$(H$_2$O)$_2$], the extreme sensitivity to spark of LA (0.0047 J) and LS (0.0002 J) are exceedingly dangerous because normal human activity can generate a static discharge up to 0.25 J. LS is known to have the worst spark sensitivity of all primary explosives. LA is as sensitive to impact when it is wet as dry, and

Table 1. Physical property, sensitivity, and explosive performance of lead and lead-free primary explosives

Explosive	DSC exo., °C	OB_{CO}	Impact, cm	Friction, g	Spark, J	Density. g/cm^3	V_D, km/sec
NH$_4$FeNT	255	0.00	12	2,800	>0.36	2.2	7.7
NaFeNT	250	5.39	12	20	>0.36	2.2	NA
NH$_4$CuNT	265	0.00	12	500	>0.36	2.0	7.4
NaCuNT	259	5.32	12	40	>0.36	2.1	NA
LA	315	0.00	10*	6	0.0047	4.8	5.5
LS	282	5.33	14	40	0.0002	3.0	5.2

NA, not available. See *Data Analysis* under *Methods*.
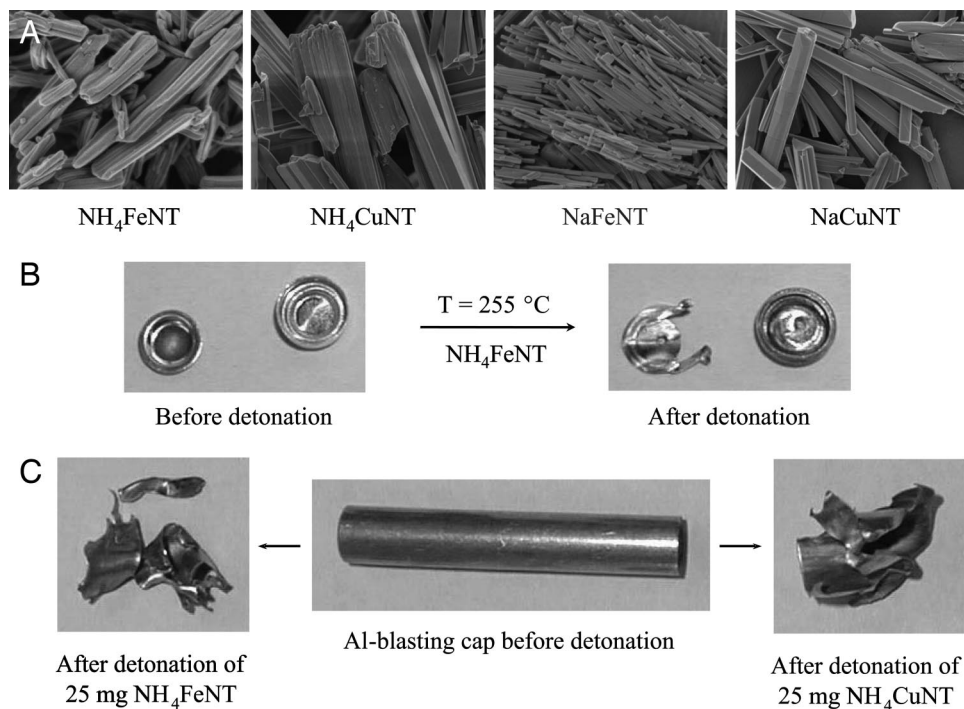*See ref. 12.

Fig. 2. Green primaries and their representative tests. (*A*) SEM images for NH₄FeNT, NH₄CuNT, NaFeNT, and NaCuNT. (*B*) Lid and sample holder from a 0.75-mg differential scanning calorimetry experiment. (*C*) Aluminum blasting cap from an experiment initiated by an electric match.

furthermore, 1-mm-long crystals of LA are vulnerable to spontaneous explosion because of internal crystal stresses (ref. 12, pp. 424–430). Even though LA is in high demand, unexpected accidents due to its extreme sensitivity prevent it from being manufactured in the U.S.
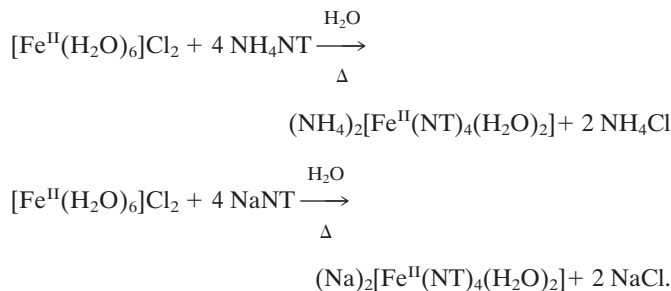
MK1 electric and M55 stab detonators were used to screen the viability of the samples as primary explosives. A comparison between LA-MK1 and NaMNT-MK1 electric detonators shows that both LA and LS are completely replaceable by NaMNT. In the NaMNT-M55 stab detonator, NaMNT replaces all LA in the transfer charge. The initiation efficiency and reliable detonation of NaMNT compared with lead primary explosives in these representative detonators were measured and confirmed by the dents on the hardened steel disk tests.

The extreme sensitivities and toxicity of LA and LS have made their application in initiating devices, which are presently manufactured in tens of millions of devices annually, increasingly controversial. The $(Cat)_2[M^{II}(NT)_4(H_2O)_2]$ salts described here are the only technologically advanced materials that meet all current criteria for green primary explosives and hold great promise as lead replacements in detonators because they (*i*) are synthesized by a green process that generates innocuous waste by-products (H_2O, NaCl, or NH₄Cl, and $NaNO_3$ or NH_4NO_3), (*ii*) have controllable explosive sensitivities allowing for mitigation of unexpected accidents, and (*iii*) deposit undisruptive decomposition products (iron or copper, N_2, CO_2, H_2O, ≈2% of NO_2, and ≈3% of CO) to the environment, avoiding the heavy metal contamination that is of increasingly serious health concern.

Methods

Synthesis of NaMNT. A solution of 1.00 g (7.30 mmol) of sodium 5-nitrotetrazolate (22) in 20 ml of water was slowly added to a 30-ml solution of 0.424 g (1.82 mmol) of $Cu^{II}(NO_3)_2 \cdot 2\frac{1}{2}(H_2O)$ with stirring. The blue suspension was slowly brought to reflux for 5 h. The clear solution then was slowly cooled to 10°C at the rate of 3°C/min and maintained at this temperature until the

solution became colorless. Most of the mother liquor was decanted; the crystals were filtered, washed with cold water, and air-dried. The preparation procedure for NH₄FeNT, NH₄CuNT, or NaFeNT is similar to that of NaCuNT, except that the appropriate salt of 5-nitrotetrazole and corresponding metal hydrate salt was used.

$$[Fe^{II}(H_2O)_6]Cl_2 + 4\ NH_4NT \xrightarrow[\Delta]{H_2O}$$

$$(NH_4)_2[Fe^{II}(NT)_4(H_2O)_2] + 2\ NH_4Cl$$

$$[Fe^{II}(H_2O)_6]Cl_2 + 4\ NaNT \xrightarrow[\Delta]{H_2O}$$

$$(Na)_2[Fe^{II}(NT)_4(H_2O)_2] + 2\ NaCl.$$

Los Alamos is at the elevation of 7,500 ft and atmospheric pressure of 580 torr (1 torr = 133 Pa) [11.2 psi (1 psi = 6.89 kPa) or 0.76 atm (1 atm = 101.3 kPa)]. Humidity is normally low.

Characterizations. *NH₄FeNT.* Anal. calcd for FeC₄H₁₂N₂₂O₁₀: C, 8.22; H, 2.07; N, 52.75; O, 27.39 and found: C, 8.29; H, 1.79; N, 48.96; O, 27.62; IR (cm⁻¹, nujol): $\nu(NO_2)$ = 1,569, 1,497, 1,455, and 1,435 cm⁻¹; $\nu(H_2O)$ = 3,537 and 3,480 cm⁻¹; $\nu(NH_4)$ = 3,300 and 3,255 cm⁻¹; ν(tetrazolate) = 1,377, 1,327, 1,256, 1,064, 846, and 667 cm⁻¹; yield: 96%.

NH₄CuNT. Anal. calcd for CuC₄H₁₂N₂₂O₁₀: C, 8.12; H, 2.04; N, 52.07; O, 27.03 and found: C, 8.06; H, 1.80; N, 48.65; O, 27.73; b) IR (cm⁻¹, nujol): $\nu(NO_2)$ = 1,564, 1,494, 1,444, and 1,442 cm⁻¹; $\nu(H_2O)$ = 3,562 and 3,465 cm⁻¹; $\nu(NH_4)$ = 3,297 and 3,255 cm⁻¹; ν(tetrazolate) = 1,378, 1,326, 1,233, 1,063, 843, and 665 cm⁻¹; yield: 93%.

NaFeNT. Anal. calcd for Na₂FeC₄H₄N₂₀O₁₀: C, 8.09; H, 0.68; N, 47.16; and found: C, 8.22; H, 0.74; N, 46.97; IR (cm⁻¹, nujol):
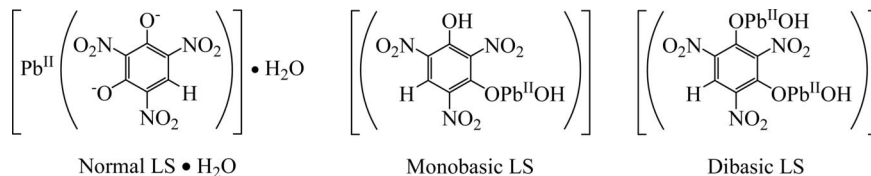
Scheme 1.

$\nu(NO_2)$ = 1,566, 1,459, 1,454, and 1,435 cm^{-1}; $\nu(H_2O)$ = 3,531 and 3,480 cm^{-1}; ν(tetrazolate) = 1,377, 1,333, 1,265, 1,067, 845, and 667 cm^{-1}; yield: 92%.

NaCuNT. Anal. calcd for Na$_2$CuC$_4$H$_4$N$_{20}$O$_{10}$: C, 7.98; H, 0.67; N, 46.56 and found: C, 8.02; H, 0.72; N, 46.55; b) IR (cm^{-1}, nujol): $\nu(NO_2)$ = 1,564, 1,461, 1,445, and 1,433 cm^{-1}; $\nu(H_2O)$ = 3,482 and 3,390 cm^{-1}; ν(tetrazolate) = 1,379, 1,326, 1,235, 1,066, 841, and 663 cm^{-1}; yield: 94%.

Materials. *LS.* Mono- and dibasic LS are two other important lead salts of styphnic acid. Their thermal stability of 295 ± 5°C is slightly higher than that of the normal LS, but their sensitivity properties, explosive performance, and applications in initiating devices are comparable with those of normal LS (see Scheme 1). *LA.* It is the distinctive primary explosive that cannot be desensitized even when it is wet with water. The sensitivity data provided in this work were presumably measured by using dry LA.

Data Analyses. Oxygen balance (OB_{CO}) is an index of the deficiency or excess of oxygen in a compound required to convert all C to CO, all H to H$_2$O, all alkaline metal to A$_2$O, and all transition metals to metal oxides. This oxygen measurement is reported in percent. For a compound with the molecular formula of C$_a$H$_b$N$_c$O$_d$A$_e$M$_f$, OB_{CO} (%) = 1,600[(d-a-½b-½e-f) FW^{-1}] (A, alkaline metal, M, transition metal). From Table 1, because the density and OB_{CO} of NaMNT are higher than those of NH$_4$MNT, NaMNT presumably has at least the same or better performance (V_D and P_{CJ}) than NH$_4$MNT.

Methods of Testing. We followed Military Standard 1751 A: Department of Defense Test Method Standard and Safety and Performance Tests for the Qualification of Explosives (High Explosives, Propellants, and Pyrotechnics) issued in 1982. All detonator tests in this work were performed at U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ.

Sensitivity Measurements. *Impact test.* For the ammonium complexes, their impact sensitivity also was measured by using a drop-weight machine or a drop-hammer, type 12 test. Impact sensitivity is an average height in centimeters at which a 2.5-kg weight is dropped onto a 40-mg sample of an explosive on 150-grit garnet sandpaper. The sample detonated if a sound level of 120 dB recorded from a microphone set 33 inches from the point of initiation. The test results are summarized as H_{50}, the height in centimeters at which the probability of explosion is 50%.

Friction test. Friction sensitivity was determined by a mini Federal Institute for Materials Research and Testing (BAM) machine capable of measuring from 0 to 1,000 g. In each test, a rounded porcelain striker ground to set off 1 mg of explosive on a porcelain plate that is mechanically driven directly underneath the striker at a given weight. The striker was pivotal to a calibrated arm on which different weights can be hung. The criterion for detonation was an audible or visual reaction or both recognized by an operator. The test results are statistically reported as a 50% load with the explosive probability of 50%.

Spark test. Spark sensitivity from 0 to 6 J was measured by Allegany Ballistics Laboratory electrostatic discharge apparatus connected to a diagnostic analyzer to detect NOX, CO (0–5,000 ppm), and CO$_2$ (0–1,000 ppm) released from a detonated sample. In an insulating plastic disk sat on a conductive steel base, a 2- to 3-mg sample was covered with a piece of Scotch tape (3M Co.), and the assembly was centralized beneath a brass needle that would be charged when the instrument was initiated. This charged needle pierced through the Scotch tape, discharging the spark to set off the sample. The spark energy of the explosive sample was sent to the analyzer and recorded in joules.

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