

Green primary explosives: 5-Nitrotetrazolato- N^2 -ferrate hierarchies

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The sensitive explosives used in initiating devices like primers and detonators are called primary explosives. Successful detonations of secondary explosives are accomplished by suitable sources of initiation energy that is transmitted directly from the primaries or through secondary explosive boosters. Reliable initiating mechanisms are available in numerous forms of primers and detonators depending upon the nature of the secondary explosives. The technology of initiation devices used for military and civilian purposes continues to expand owing to variations in initiating method, chemical composition, quantity, sensitivity, explosive performance, and other necessary built-in mechanisms. Although the most widely used primaries contain toxic lead azide and lead styphnate, mixtures of thermally unstable primaries, like diazodinitrophenol and tetracene, or poisonous agents, like antimony sulfide and barium nitrate, are also used. Novel environmentally friendly primary explosives are expanded here to include $\text{cat}[\text{Fe}^{\text{II}}(\text{NT})_3(\text{H}_2\text{O})_3]$, $\text{cat}_2[\text{Fe}^{\text{II}}(\text{NT})_4(\text{H}_2\text{O})_2]$, $\text{cat}_3[\text{Fe}^{\text{II}}(\text{NT})_5(\text{H}_2\text{O})]$, and $\text{cat}_4[\text{Fe}^{\text{II}}(\text{NT})_6]$ with cat = cation and NT^- = 5-nitrotetrazolato- N^2 . With available alkaline, alkaline earth, and organic cations as partners, four series of 5-nitrotetrazolato- N^2 -ferrate hierarchies have been prepared that provide a plethora of green primaries with diverse initiating sensitivity and explosive performance. They hold great promise for replacing not only toxic lead primaries but also thermally unstable primaries and poisonous agents. Strategies are also described for the systematic preparation of coordination complex green primaries based on appropriate selection of ligands, metals, and synthetic procedures. These strategies allow for maximum versatility in initiating sensitivity and explosive performance while retaining properties required for green primaries.

iron complex primary | nitrotetrazolate anion | high-nitrogen ligand | environmentally friendly | highly sensitive

Primary high explosives are the sensitive explosives used in initiating devices such as primers and detonators for commercial and military applications. As mentioned in a recent report (1) and in two patent applications (2, 3), toxic mercury fulminate (MF) (4) has been used as an initiating primary since 1628 (5). Lead azide (LA) (6) and lead styphnate (LS) (7), identified in 1907, are the only viable primary replacements, but their deleterious environmental impacts and effects on human health have made their replacement essential (1). Even after nearly 400 years of research, appropriate replacements for MF having acceptable stability, sensitivity, and suitable explosive performance remained elusive until our recent reports of new coordination complex primary explosives (1–3).

Countless numbers of energetic compounds have been designed and screened as possible primaries, including organic compounds, organic salts, zwitterions, simple inorganic salts, coordination complexes, and metastable interstitial composites (MICs). Heretofore, none have simultaneously met the six green primary criteria: (i) insensitive to moisture and light; (ii) sensitive to initiation 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, (1), which may be a possible teratogen and has adverse effects on thyroid function (8). Clearly, new approaches are needed.

Developing qualified primaries is much like searching for effective drugs or creating efficient catalysts. Just as energetic materials chemists manipulate chemical functionality to obtain desirable sensitivity and choose molecular backbones to improve explosive performance, pharmacologists try different building blocks to search for treatment and change substituents on parent compounds to minimize side effects, and coordination chemists judiciously select metals as well as ligands to design inexpensive catalysts and then fine-tune reaction conditions to maximize products. Fundamentally, most scientific researchers operate on the same principles to accomplish different missions.

We present here a versatile interdisciplinary approach to the design of green primaries prepared from four distinct series of 5-nitrotetrazolato- N^2 -ferrate coordination complex anions, $[\text{Fe}^{\text{II}}(\text{NT})_3(\text{H}_2\text{O})_3]^-$ ($[\text{Fe}^{\text{II}}\text{NT}_3]^-$), $[\text{Fe}^{\text{II}}(\text{NT})_4(\text{H}_2\text{O})_2]^{2-}$ ($[\text{Fe}^{\text{II}}\text{NT}_4]^{2-}$),¹ $[\text{Fe}^{\text{II}}(\text{NT})_5(\text{H}_2\text{O})]^{3-}$ ($[\text{Fe}^{\text{II}}\text{NT}_5]^{3-}$), and $[\text{Fe}^{\text{II}}(\text{NT})_6]^{4-}$ ($[\text{Fe}^{\text{II}}\text{NT}_6]^{4-}$), and numerous cations including alkaline, alkaline earth, aliphatic and heterocyclic nitrogen compounds (9), and their catenated derivatives (10). These resulting coordination complex primaries are thermally stable to >250°C, possess controllable sensitivities, are stable to light and moisture, and contain no toxic metals or perchlorate.

Results

As mentioned in our recent communication (1), the salts $\text{cat}_2[\text{M}^{\text{II}}(\text{NT})_4(\text{H}_2\text{O})_2]$ with $\text{cat} = \text{NH}_4^+$ or Na^+ and $\text{M} = \text{Fe}(\text{II})$ or $\text{Cu}(\text{II})$ meet all six criteria for green primaries. To take full advantage of this metal–ligand combination, we have systematically varied the number of the NT^- ligands to customize explosive performance and the cation to control sensitivity. This approach leads to a diverse and flexible suite of salts based on the 5-nitrotetrazolato- N^2 -ferrates $[\text{Fe}^{\text{II}}\text{NT}_3]^-$, $[\text{Fe}^{\text{II}}\text{NT}_4]^{2-}$, $[\text{Fe}^{\text{II}}\text{NT}_5]^{3-}$, and $[\text{Fe}^{\text{II}}\text{NT}_6]^{4-}$ and the monocations sodium (Na^+), nitrosocyanaminium (NCam) (11), ammonium (NH_4^+), hydrazonium (Hyzm), 1,2,5-triamino-1,2,3-triazolium (TATm) (12), and 5-amino-1-nitroso-1,2,3,4-tetrazolium (ANTm) (13) shown in Fig. 1.

The salts $\text{cat}[\text{Fe}^{\text{II}}\text{NT}_3]$ and $\text{cat}_2[\text{Fe}^{\text{II}}\text{NT}_4]$ were prepared from stoichiometric amounts of catNT (14) and the $\text{Fe}(\text{II})$ salt $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]\text{Cl}_2$ in refluxing water with stirring for 2 h (1). The preparations of the salts $\text{cat}_3[\text{Fe}^{\text{II}}\text{NT}_5]$ and $\text{cat}_4[\text{Fe}^{\text{II}}\text{NT}_6]$ were similar except that absolute ethanol was used as the solvent (3). After filtration, the products were washed with fresh solvent and air-dried. The products were obtained in nearly quantitative yield and were analytically pure.

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Abbreviation: OBco, combination of oxygen balance.

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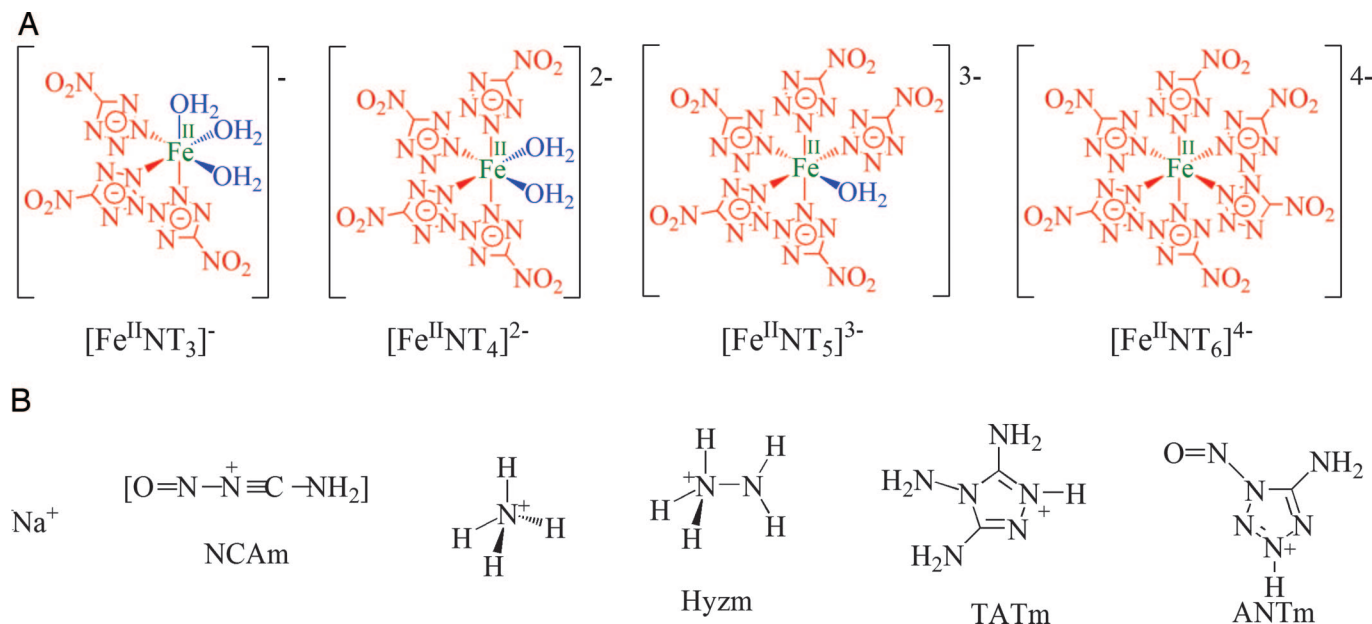


Fig. 1. Inorganic green primary explosives. (Upper) 5-Nitrotetrazolato-*N*²-ferrate coordination complex anions. (Lower) Representative cations.

These green primaries are insensitive to spark regardless of cation even when dry. When wet by common organic solvents or water, they become insensitive to friction and impact and have no response to an open flame. This ease of desensitization makes them safe to prepare, store, handle, and transport (1). Before use, they are air-dried at room temperature. These primaries are sparingly soluble in most common organic solvents and water, structurally stable to light and moisture, and thermally stable to >250°C.

The oxygen-rich NT⁻ ligands contribute sensitivity and explosive energy to the coordination complex anions; thus, the green primaries with the greater number of NT⁻ ligands are more sensitive and have better explosive performance (15). Explosive performance is determined by a combination of oxygen balance (OB_{CO}), density (ρ), and heat of formation (ΔH_f). In general, the explosive performance is enhanced by increasing OB_{CO}, ρ , and ΔH_f . For the coordination complex anions, OB_{CO} is +10.62% for $[\text{Fe}^{\text{II}}\text{NT}_3]^-$, +11.68 for $[\text{Fe}^{\text{II}}\text{NT}_4]^{2-}$, +12.42 for $[\text{Fe}^{\text{II}}\text{NT}_5]^{3-}$, and +12.97 for $[\text{Fe}^{\text{II}}\text{NT}_6]^{4-}$. When the fuel-rich NH₄⁺ cations are replaced by Na⁺, OB_{CO} values significantly increase, e.g., +3.40 → +8.42 for $[\text{Fe}^{\text{II}}\text{NT}_3]^-$, 0.00 → +8.08 for $[\text{Fe}^{\text{II}}\text{NT}_4]^{2-}$, -2.29 → +7.85 for $[\text{Fe}^{\text{II}}\text{NT}_5]^{3-}$, and -3.94 → +7.69 for $[\text{Fe}^{\text{II}}\text{NT}_6]^{4-}$.

Regardless of the number of NT⁻ ligands, the green primaries with sodium cations detonate when exposed to an open flame. With ammonium cations, they undergo deflagration-to-detonation transition (DDT). Given the same number of NT⁻ ligands, the green primaries with sodium cations are always more sensitive to friction and impact than their corresponding ammonium analogues.

Discussion

Given the advanced development of initiation devices and the current criteria for green primaries, the keys to success in developing green primaries include not only skill and knowledge but also flexibility and creativity to address the balance among safety, sensitivity, performance, stability, and nontoxicity. We present here a strategy based on relationships and properties of high explosives and synthetic versatility.

Relationships and Properties of High Explosives. An explosive is defined as a substance that releases energy (16) upon initiation by either heat, flame, shock (17), impact (18), friction (19), or spark (20) to form more stable materials. Its maximum lethality is measured by the total energy (16) generated by a sudden outburst of gas, abrupt liberation of heat, and brusque development of pressure delivered to a target. Although there are three fundamental types of modern military and commercial explosives (mechanical, chemical, and atomic explosives) (21), our focus will be restricted to chemical explosives. Chemical explosives are further categorized into low explosives (deflagrating explosives) that rapidly burn at lower pressure and high explosives (detonating explosives) that instantaneously detonate at high pressure.

High explosives are subcategorized into primary high explosives (primaries) and secondary high explosives (secondaries). Brisance, power, and detonation velocity are the most important criteria for secondaries whereas sensitivity and triggered velocity are vital requirements for primaries (22). Primaries are used in small quantities in initiation devices such as primers (23) and detonators (24) and are always detonated by simple ignitions such as flame, heat, friction, spark, or impact. Secondaries are detonated by an initiation device, but those with sufficiently sensitive functional groups can be detonated by spark, impact, or friction. Others, in large amount under confinement conditions, can easily be initiated by a flame or heat.

Secondaries are subdivided into sensitive and insensitive explosives, with the latter principally used as the main charge in practical applications. Owing to the insusceptibility to initiation of insensitive explosives, sensitive secondary explosives are used as explosive train boosters (25) in conjunction with primers or detonators to transmit and augment the detonation wave from the primaries to ensure a high-order detonation. The focus of our attention here will be on primaries and sensitive secondaries.

Existing Primaries. Mercury fulminate (4), lead 2-mononitroresorcinate (LMNR) (26), lead azide (6), and lead styphnate (7) in Fig. 2A are simple inorganic salts. They are thermally stable to >200°C, but their excessive sensitivity and release of toxic metals upon detonation have made their replacement desirable. An

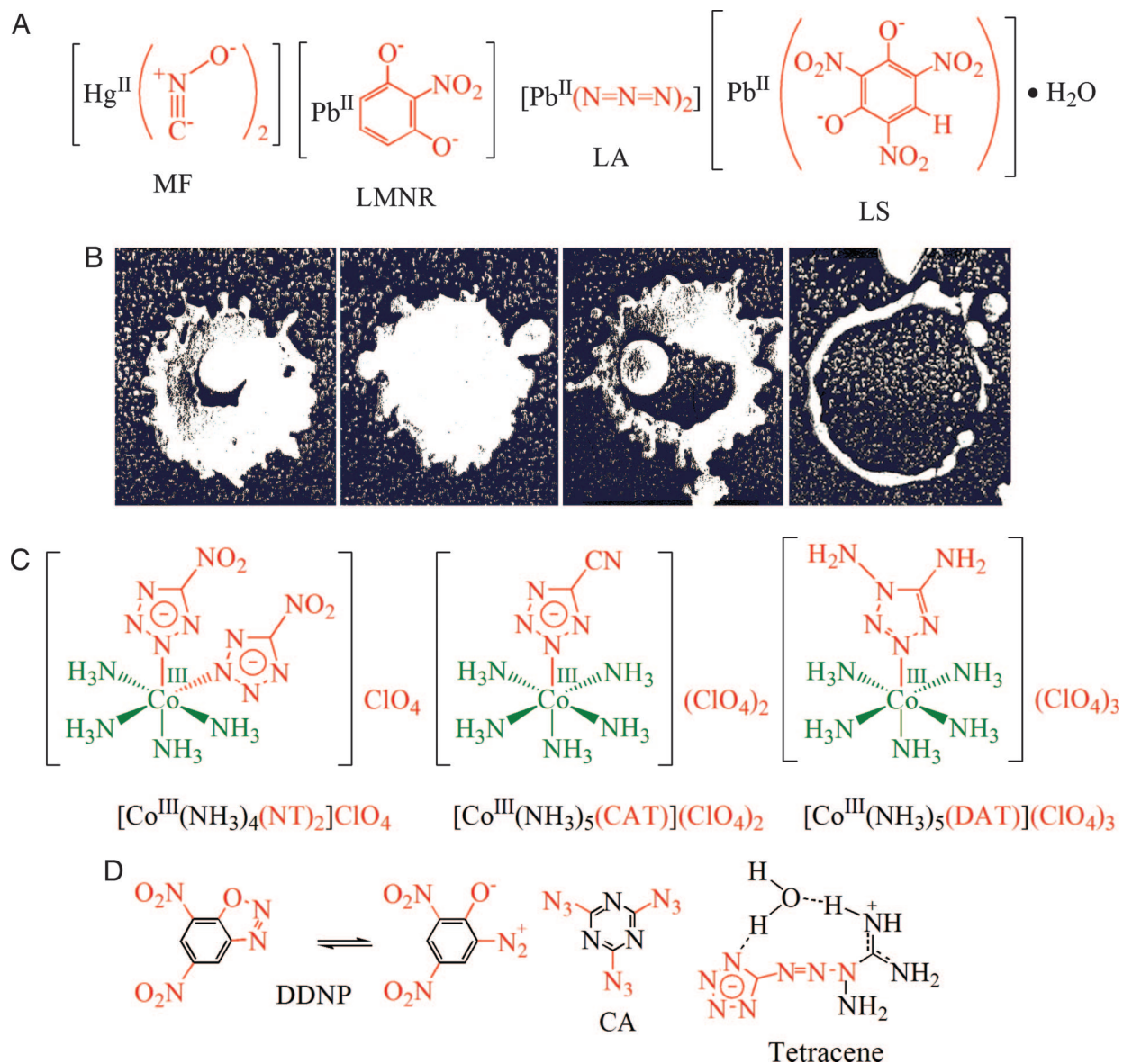


Fig. 2. Commonly used primary explosives. (A) Inorganic simple salts of mercury and lead. (B) Depositions of 50- μm lead spatter on the collecting surface at different velocities. (C) Inorganic coordination complex primaries. (D) Organic primaries.

example of toxic lead deposition from LMNR, the major ingredient in electric matches, is shown in Fig. 2B (27).

More recent examples of coordination complex primaries in Fig. 2C are tetraammine and pentaammine cobalt(III) complexes, e.g., tetraammine(5-nitrotetrazolate- N^2)cobalt(III) perchlorate ($[\text{Co}^{\text{III}}(\text{NH}_3)_4(\text{NT})_2]\text{ClO}_4$) (28), pentaammine(5-cyanotetrazolate- N^2)cobalt(III) perchlorate ($[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{CAT})](\text{ClO}_4)_2$) (29), and pentaammine(5-aminotetrazolate- N^2)cobalt(III) perchlorate ($[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{DAT})](\text{ClO}_4)_3$) (30). Their sensitivity and performance can be varied with the number of perchlorate groups; however, perchlorate is a possible teratogen and has adverse effects on thyroid function (8). Furthermore, dermatitis, asthma, dyspnea, respiratory hypersensitivity, and diffuse nodular fibrosis are potential symptoms from overexposure to deposited cobalt metal (which results from detonation of these cobalt primaries) (31) even though the cobalt(III)ammine coordination complex cations are not toxic (32).

Diazodinitrophenol (DDNP), cyanuric triazide (CA), and tetracene in Fig. 2D are well known organic primaries (1).

Unfortunately, these primaries are not stable upon exposure to heat and light and lack the required thermal stability. In addition, DDNP activates an inappropriate immune system response that predisposes toward allergic syndromes (33). In enclosed rifle ranges, personnel are under health risk because of the use of SINTOX compositions, which are mixtures of DDNP, tetracene, zinc peroxide, and titanium (34).

Versatile Synthesis of Green Primaries. As mentioned above, the $(\text{cat})_x-2[\text{M}^{\text{II}}(\text{NT})_x(\text{H}_2\text{O})_{6-x}]$ architecture meets all of the criteria for green primaries. In these coordination complex primaries, the coordination complex anions are the primary oxygen carrier as well as the sensitivity bearer whereas the cationic partner allows selective fine-tuning of sensitivity for various applications.

Selecting Ligands. Similar to the perchlorate counter anions of the tetraammine and pentaammine cobalt(III) complexes, the ligands must be oxygen-rich, sensitive, secondary high explosive anions because they must provide oxygen content and sensitivity

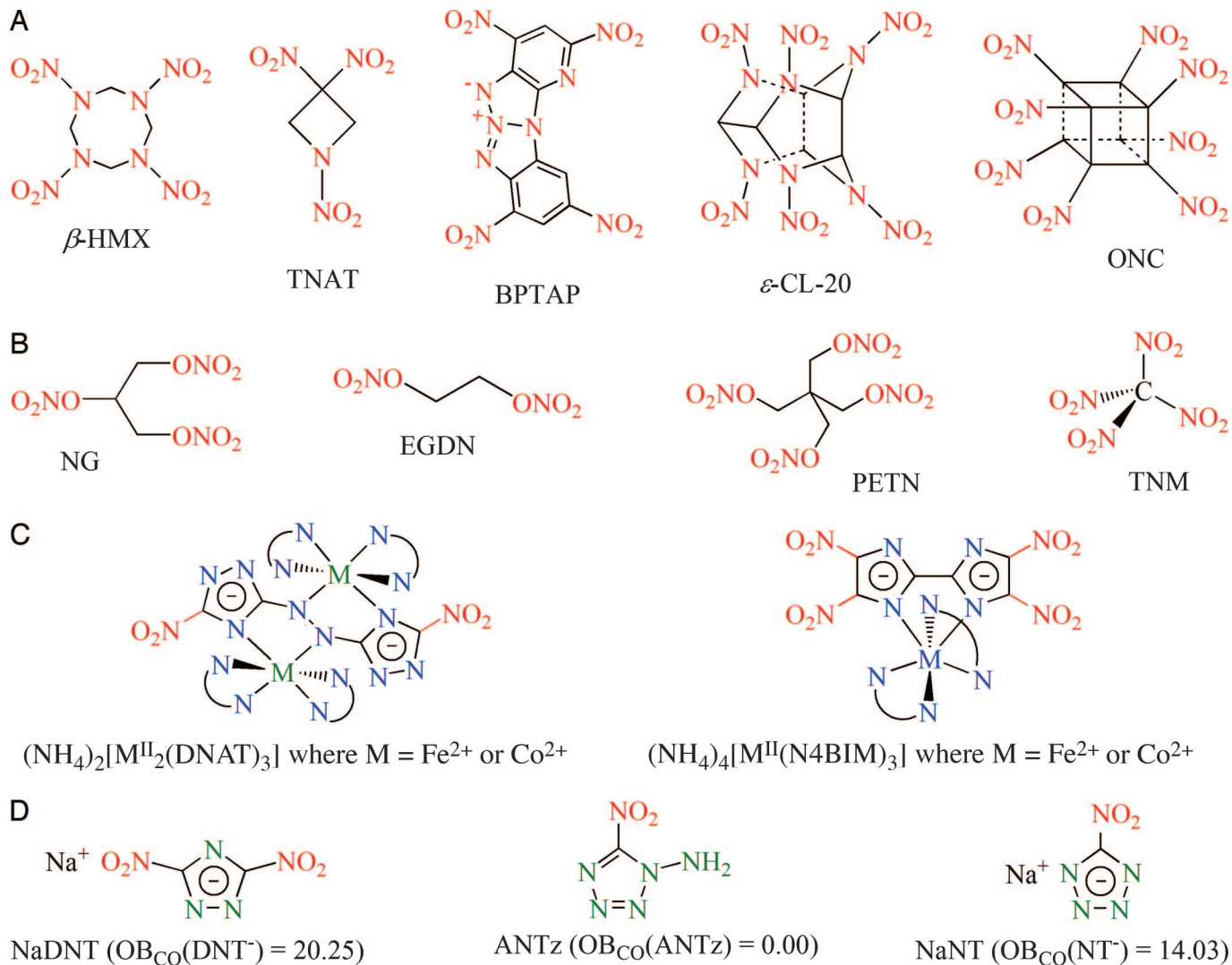


Fig. 3. Prospective organic explosives for ligand consideration. (A) Ring-strained nitro compounds. (B) Aliphatic N-based nitro compounds. (C) Complexes with oxygenic bidentate ligands. (D) Heterocyclic nitro compounds.

to the metal complex anions. To be methodical, a judicious collection of various oxygen-rich, sensitive secondary high explosives was investigated. Ring-strained nitro compounds (15) {e.g., octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (β -HMX or octogen); 1,3,3-trinitroazetidine (35); 2,4-diazido-3,8,10-trinitro-5H-pyrido-[3',2':4,5][1,2,3]triazolo[1,2-a]benzotriazol-6-ium inner salt (BPTAP) (36); 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaza-tetracyclo[5.5.0.0.5,9.0.3,11]-dodecane (ϵ -CL-20); and octanitrocubane} have outstanding explosive performance and suitable sensitivity, but, unfortunately, they cannot be ligands, owing to the lack of appropriate atom donors (Fig. 3A) (15).

Aliphatic nitro compounds in Fig. 3B [e.g., glycerol trinitrate (NG) (37); ethyleneglycol dinitrate (EGDN) (38); pentaerythritol tetranitrate (PETN); and tetranitromethane] are powerful explosives owing to their highly positive OB_{CO} ; however, they are not able to coordinate to the metals.

First-row transition metal complexes coordinated by oxygen-rich bidentate ligands such as 5,5'-dinitro-3,3'-azo-1,2,4-triazolate (DNAT^{2-}) (39) and 4,4',5,5'-tetranitro-2,2'-biimidazole (N4BIM) exhibit insensitivities to spark, friction, and impact (40). In our experience, $(\text{NH}_4)_2[\text{Cu}^{\text{II}}_2(\text{DNAT})_3]$, $(\text{NH}_4)_2[\text{Fe}^{\text{II}}_2(\text{DNAT})_3]$, $(\text{NH}_4)_2[\text{Co}^{\text{II}}_2(\text{DNAT})_3]$, $(\text{NH}_4)_4$

$[\text{Fe}^{\text{II}}(\text{N4BIM})_3]$, and $(\text{NH}_4)_4[\text{Co}^{\text{II}}(\text{N4BIM})_3]$ have high explosive performance, but the chelation effect of the bidentate DNAT^{2-} and N4BIM^{2-} ligands makes their complexes too insensitive to be considered primary explosives, Fig. 3C.

Monosubstituted anions of tetrazole and disubstituted anions of triazole are well known to be favorable N-ligands for transition metals. Comparison of 1-amino-5-nitrotetrazole (ANTz) (41) to NT^- reveals the latter to be the more energetic ligand because of its more positive OB_{CO} (14.03 versus 0.00) and higher energy content. Although 3,5-dinitro-1,2,4-triazolate- N^{2-} (DNT^-) (42) has higher OB_{CO} (20.25) than NT^- (14.03), the influence of the two-electron-withdrawing nitro groups limits its ability to coordinate to transition metals (Fig. 3D).

Table 1. Cationic dependence of representative OB_{CO}

Cation	Primary			
	$[\text{Fe}^{\text{II}}\text{NT}_3]^-$	$[\text{Fe}^{\text{II}}\text{NT}_4]^{2-}$	$[\text{Fe}^{\text{II}}\text{NT}_5]^{3-}$	$[\text{Fe}^{\text{II}}\text{NT}_6]^{4-}$
None	+10.62	+11.68	+12.42	+12.97
NH_4^+	+3.40	0.00	-2.29	-3.94
Na^+	+8.42	+8.08	+7.85	+7.69

Table 2. Selected properties and sensitivities of ammonium 5-nitrotetrazolato-*N*²-ferrate hierarchies

Properties	Primary			
	NH ₄ [Fe ^{II} NT ₃]	(NH ₄) ₂ [Fe ^{II} NT ₄]	(NH ₄) ₃ [Fe ^{II} NT ₅]	(NH ₄) ₄ [Fe ^{II} NT ₆]
ρ , g/cm ³	2.10 ± 0.02	2.20 ± 0.03	2.34 ± 0.02	2.45 ± 0.02
DSC exo., °C	261	255	253	252
Spark, J	>0.36	>0.36	>0.36	>0.36
Friction, kg	4.2	2.8	1.3	0.8
Impact, cm	15	12	10	8

DSC exo., Differential scanning calorimetry exotherm performed with the rate of 5°C/min.

Among the first-row transition metals, the DNT⁻ ligand only coordinates to copper(II), [Cu^{II}(H₂O)₆](NO₃)₂, to form *trans*-[Cu^{II}(H₂O)₄(DNT)₂] *in situ*. The addition of concentrated ammonium hydroxide gives an isolable product, *trans*-[Cu^{II}(NH₃)₄(DNT)₂] (43). The 5-substituted tetrazolate derivatives, including the poor electron-donating 5-trifluoromethyltetrazolate ligand, are well known as excellent ligands (44). Among oxygen-rich, energetic ligands with high-energy content, NT⁻ is far superior to all sensitive secondary high explosives yet tested.

Choosing the Metal Center. The stability exhibited by transition metal complexes primarily depends on the oxidation state of the metal, geometrical arrangements of ligands around the metal, and stereoelectronic (steric and electronic) effects of the ligands (45). Iron is particularly advantageous because it has a predictable octahedral geometry in many coordination environments and in both Fe(II) and Fe(III). It is also highly labile, allowing fast reactions that are commercially advantageous. Lastly, it is both biologically required and environmentally friendly, so deposition of iron metal poses no risk to the environment or personnel.

Choosing Complexes with Maximum Versatility. In the *cis*-[Co^{III}(NH₃)₄(NT)₂]ClO₄ complex, the Co(III) center is coordinated to two NT⁻s with the charge counterbalanced by one ClO₄⁻. In our green primaries, the Fe(II) metal center is consecutively coordinated with three, four, five, and six NT⁻s to give [Fe^{II}(H₂O)₃(NT)₃]⁻, [Fe^{II}(H₂O)₂(NT)₄]²⁻, [Fe^{II}(H₂O)(NT)₅]³⁻, and [Fe^{II}(NT)₆]⁴⁻ with charges offset by one, two, three, and four cations, respectively. This logical extension creates a series of green Fe-based hierarchies with incremental explosive performance and initiating sensitivities. Table 1 shows how the cationic partners are manipulated to fine-tune sensitivity and susceptibility to initiation, and Table 2 illustrates how the number of NT⁻ ligands can be adjusted to enhance sensitivity and explosive performance for the ammonium primaries.

Energetically, NT⁻ is the best ligand for energetic coordinated anionic complexes because it possesses a very high positive ΔH_f as a result of its inherently energetic N—N and C—N bonds. Compared with all other heterocyclic five- and six-member rings, the NT⁻ ligand has much higher potential energy content because of the tetrazole backbone and the nitro group.

As shown in Table 2, the densities of four ammonium 5-nitrotetrazolato-*N*²-ferrate hierarchies increase as the number of NT⁻s increases. Reminiscent of [Fe^{II}(ClCH₂CH₂-Tz)₆](BF₄)₂ (46), six 1-(2-chloroethyl)tetrazole-*N*⁴ ligands are well packed within each other as a result of the slanting and wedging of the five-member aromatic planarity (46). The conversion of the neutral 5-aminotetrazole to the negatively charged 5-nitrotetrazolate increases the density, which improves explosive performance, and enhances the initiating sensitivity.

Conclusion

In contrast to current primary explosives, including simple inorganic salts, inorganic coordination complexes with metallic cations, organic compounds, and metastable interstitial composites, the 5-nitrotetrazolato-*N*² ferrate hierarchies meet all requirements for green primary explosives. They hold great promise for replacing toxic lead and thermally unstable primaries as a result of the diversity in their explosive performance and initiating sensitivity.

Compared with existing primaries, they are easier to prepare, safer to handle, and more convenient to transport because they are completely insensitive when wet with water. They are resistant to decomposition upon exposure to moisture, light, or heat, and they are stable to intramolecular rearrangement and ligand exchange. Once isolated, they are insoluble and stable to most common organic solvents and water. They are stable to at least 250°C for extended periods, and they release nontoxic metal and harmless gaseous by-products to the environment upon detonation.

Methods

Synthesis of (Na)₂[Fe^{II}(NT)₃(H₂O)₃]. A solution of 1.00 g (7.30 mmol) of sodium 5-nitrotetrazolate (14) in 20 ml of water was slowly

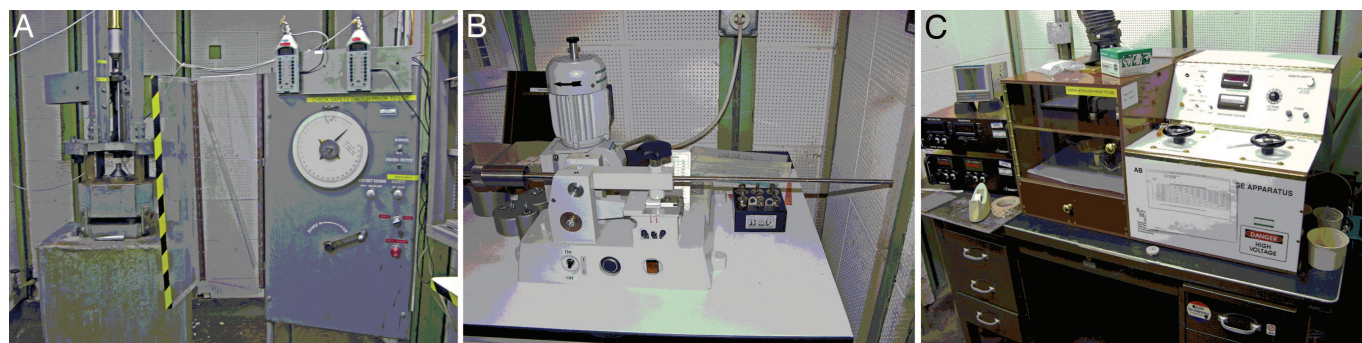


Fig. 4. Instruments for sensitivity tests. (A) Drop-weight impact machine. (B) Mini BAM friction machine. (C) ABL electrostatic discharge.

added to a 30-ml solution of 0.571 g (1.82 mmol) of $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]\text{Cl}_2$ with stirring. The orange suspension was slowly brought to reflux for 2 h. The clear solution was then 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 procedures for $\text{Na}_3[\text{Fe}^{\text{II}}(\text{NT})_5(\text{H}_2\text{O})]$ and $\text{Na}_4[\text{Fe}^{\text{II}}(\text{NT})_6]$ are similar to that of $\text{Na}[\text{Fe}^{\text{II}}(\text{NT})_3(\text{H}_2\text{O})_3]$, except that absolute ethyl alcohol was used as the solvent. Their derivatives with different cationic partners are analogously prepared with the appropriate salt of 5-nitrotetrazolate and $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]\text{Cl}_2$ (1).

Characterizations. $\text{NH}_4[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_3(\text{NT})_3]$. (i) Anal. Calcd for $\text{FeC}_3\text{H}_{10}\text{N}_{16}\text{O}_9$: C, 7.67; H, 2.14; N, 47.68; O, 30.63 and found: C, 7.82; H, 2.08; N, 45.20; O, 30.45; (ii) IR (cm^{-1} , Nujol): $\nu(\text{H}_2\text{O}) = 3,540, 3,480, \text{ and } 3,475 \text{ cm}^{-1}$; $\nu(\text{NH}_4) = 3,252 \text{ cm}^{-1}$; $\nu(\text{NO}_2) = 1,571, 1,497, 1,456, \text{ and } 1,442 \text{ cm}^{-1}$; $\nu(\text{Tetrazolate}) = 1,377, 1,326, 1,169, 1,065, 845, \text{ and } 667 \text{ cm}^{-1}$; and (iii) yield: 95%. $(\text{NH}_4)_3[\text{Fe}^{\text{II}}(\text{H}_2\text{O})(\text{NT})_5]$. (i) Anal. Calcd for $\text{FeC}_5\text{H}_{14}\text{N}_{28}\text{O}_{11}$: C, 8.60; H, 2.02; N, 56.17; O, 25.21 and found: C, 8.71; H, 1.96; N, 55.12; O, 25.49; (ii) IR (cm^{-1} , Nujol): $\nu(\text{H}_2\text{O}) = 3,472 \text{ cm}^{-1}$; $\nu(\text{NH}_4) = 3,306, 3,297, \text{ and } 3,252 \text{ cm}^{-1}$; $\nu(\text{NO}_2) = 1,564, 1,494, 1,463, \text{ and } 1,442 \text{ cm}^{-1}$; $\nu(\text{tetrazolate}) = 1,379, 1,326, 1,234, 1,063, 843, 665, \text{ and } 556 \text{ cm}^{-1}$; and (iii) yield: 92%. $(\text{NH}_4)_4[\text{Fe}^{\text{II}}(\text{NT})_6]$. (i) Anal. Calcd for $\text{FeC}_6\text{H}_{16}\text{N}_{34}\text{O}_{12}$: C, 8.87; H, 1.99; N, 58.63; O, 23.64 and found: C, 8.96; H, 1.89; N, 56.42; O, 23.51; (ii) IR (cm^{-1} , Nujol): $\nu(\text{NO}_2) = 1,572, 1,565, 1,501, 1,455, 1,441, \text{ and } 1,438 \text{ cm}^{-1}$; $\nu(\text{tetrazolate}) = 1,378, 1,327, 1,235, 1,166, 842, \text{ and } 665 \text{ cm}^{-1}$; and (iii) yield: 94%.

Data Analyses. 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_2O , all alkaline metals to A_2O , and all transition metallic cations to neutral metals. This oxygen measurement is reported in percent. For a compound with the molecular formula of $\text{C}_a\text{H}_b\text{N}_c\text{O}_d\text{A}_e$, $\text{OB}_{\text{CO}} (\%)$ is calculated according to $1,600[(d - a - \frac{1}{2}b - \frac{1}{2}e)\text{FW}^{-1}]$ (A = alkaline metal).

Sensitivity Measurements. The impact sensitivity for the ammonium complexes was measured by using a drop-weight machine or a drop hammer, type 12 test. Friction sensitivity was determined by a mini BAM machine (Reichel & Partner, Rheinzaubern, Germany) capable of measuring from 0 to 1,000 g. Spark sensitivity from 0 to 6 J is measured by an ABL electrostatic discharge apparatus (Safety Management Services, West Jordan, UT) connected to a diagnostic analyzer to detect NOX, CO (0–5,000 ppm), and CO_2 (0–1000 ppm) released from a sample (1). Because we provided detailed descriptions of three sensitivity tests in our previous report (1), we illustrate three instruments in Fig. 4 as follows: drop-weight impact machine (Fig. 4A), mini BAM friction machine (Fig. 4B), and the ABL electrostatic discharge machine (Fig. 4C).

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