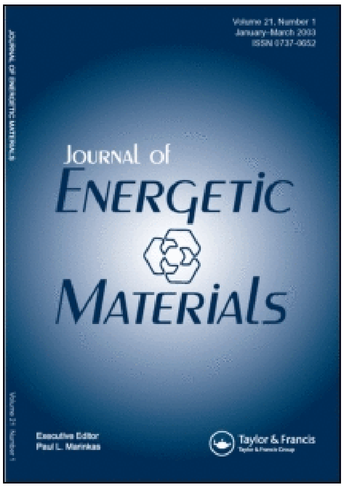

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Calcium 5-Nitriminotetrazolate—A Green Replacement for Lead Azide in Priming Charges

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Calcium 5-Nitriminotetrazolate—A Green Replacement for Lead Azide in Priming Charges

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*The new energetic material calcium 5-nitriminotetrazolate (**1**) is presented. A facile preparative route in combination with an outstanding thermal as well as long-term stability, easy initiation, and low sensitivity make **1** an auspicious green alternative filler in priming charges.*

Keywords: nitramines, primary explosives, tetrazoles, X-ray

Introduction

Research on "green" energetic materials is an ongoing project in many research groups worldwide [1–6]. All classes of energetic

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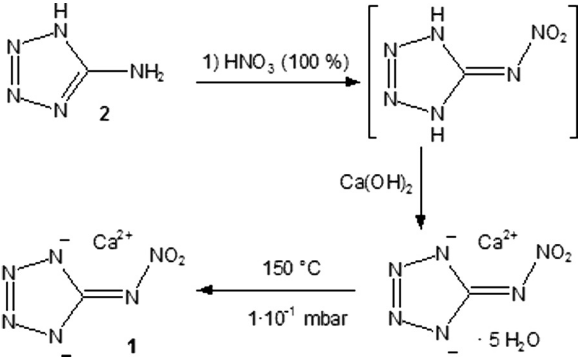
materials (explosives, propellants, pyrotechnics) contain polluting ingredients and decomposition products. Nitrogen-rich derivatives are promising alternatives as energetic materials because the formation of molecular nitrogen as an end-product of propulsion or explosion is highly desirable. These end-products avoid environmental pollution and health risks, as well as reduce plume signatures [7]. In primary explosives, the application of heavy metal salts, for example, lead azide and lead styphnate, should also be strongly reduced. Lead azide is employed as an initiating explosive in blasting caps, because it is reliable, cheap, easy to manufacture, and shows an appropriate thermal stability ($T_{\mathrm{dec.}}$: 320–340°C). When used as a primary charge, it is effective in smaller quantities than mercury fulminate [8]. Primary charges are the secondary component in ignition trains, which are designed to initiate secondary explosives; for example, trinitrotoluene (TNT) or Royal Demolition Explosive (RDX). Next to the high toxicity, lead azide is also decomposed by atmospheric CO_2 and shows high sensitivity toward impact (1–4 J) and friction (0.1–1 N). Several substitutes for lead azide have been suggested over the last decades [9]. Less toxic silver azide ($\mathrm{T_{dec}}$: 270–275°C) gives a very satisfactory initiation effect that is superior to that of $Pb(N_3)_2$. Nevertheless, its practical use is limited, because it is light sensitive and also highly sensitive toward friction. The hardest criteria for new primary explosives are a good thermal stability in combination with great performance. Zhilin et al. presented the two high-energy-capacity complexes tetraammine-*cis*-bis(5-nitro-2*H*-tetrazolato-*N*2)-cobalt(III) perchlorate [10] and tetraammine-bis(1-methyl-5-aminotetrazole-*N*3,*N*4)cobalt(III) perchlorate [11]; the first is presently used in missile manufacture and the mining industry. We also presented several replacements based on copper bis(tetrazole-5-yl)amines [12]. In this work we present our most powerful and qualified replacement for lead azide, calcium 5-nitriminotetrazolate (**1**). A facile synthetic route that can also be performed on larger scales, a comprehensive characterization including safety tests, as well as an initiation experiment are described. It is a further contribution to the promising class of 5-nitriminotetrazoles, which have been extensively described in the literature [13].

Results and Discussion

Calcium 5-nitriminotetrazole (**1**) is a powerful energetic material that shows sensitivities toward outer stimuli. Proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar gloves and earplugs) should be used when handling compound **1**. Extra safety precautions should be taken, especially when 5-nitrimino-1,4*H*-tetrazole is prepared on a larger scale.

The two step, one-pot reaction of **1** is shown in Scheme 1. In the first step 5-amino-1*H*-tetrazole (**2**) is nitrated using 100% nitric acid [14]. After pouring the reaction mixture onto ice, the solution is neutralized by the addition of calcium hydroxide. The precipitate formed is isolated and recrystallized from hot water, yielding calcium 5-nitriminotetrazolate pentahydrate ($\mathbf{1} \cdot 5\,H_2O$). The last step is dehydration at higher temperatures (150°C) and lower pressures (10^{-1} mbar), yielding anhydrous **1** [15].

A thermogravimetric (TG) curve as well as a differential scanning calorimetry (DSC) thermogram are depicted in Fig. 1 [16]. The TG curve shows that the loss of water occurs over two



Scheme 1. Preparative route to calcium 5-nitriminotetrazolate (**1**).

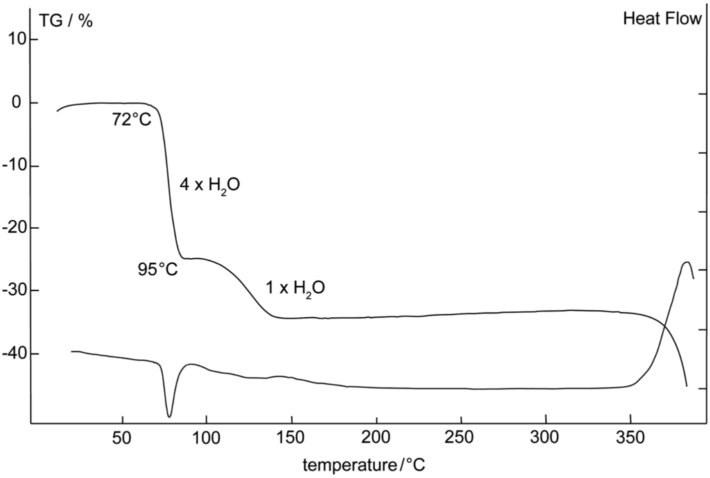


Figure 1. Thermogravimetric plot of compound **1**, showing the loss of mass (left axis, upper curve) and the differential thermal analysis (DTA) curve (right axis, lower curve).

discrete steps, which can be explained by the crystal structure. Four water molecules are lost between 72 and 85°C, which has been calculated by a loss of mass about 27%. The fifth water molecule is removed at temperatures above 92°C. Above 145°C the compound is completely dry (overall loss of mass ~35%). We performed dehydration simply by putting **1** in an oven at 200°C for 48 hr. The DSC plot demonstrates the auspicious thermal stability up to temperatures above 360°C. This decomposition temperature even surpasses that of lead and silver azide.

The structure of $\mathbf{1} \cdot 5\,H_2O$ in the crystalline state was determined by X-ray diffraction. Relevant data and parameters of the X-ray measurements and refinements are given in the references [17]. Further information on the crystal structure determination has been deposited with the Cambridge Crystallographic Data Centre [18] as supplementary publication No. 708342 ($\mathbf{1}\cdot H_2O$).

Calcium 5-nitriminotetrazolate pentahydrate crystallizes in the triclinic space group *P*-1 with two molecular moieties in the unit cell. A density of 1.89 g cm^{-3} has been calculated.

1 $\cdot$ $5H_2O$ is best described by the formation of a binuclear complex, which is depicted in Fig. 2. The 5-nitriminotetrazolate dianions coordinate by the atoms N1 and O1 to the calcium cations, forming a bite angle of 67.06(6)°. In accordance with the TG experiment four molecules of water are μ_1-coordinated, whereby one is bridging to calcium cations by a μ_2-coordination.

1 as well as its pentahydrate were investigated by several specific tests determining the energetic behavior. The sensitivities toward impact, friction, and electrical discharge have been explored by the BAM drop hammer and friction tester [19] as well as an ESD 2010EN electric spark tester (OZM Research, Bliznovice 32, Hrochuv Tynec 538 62, Czech Republic) [20]. As with other energetic materials, **1** $\cdot$ $5H_2O$ is less sensitive toward impact (75 J) than its anhydrous analogue (5 J). Also, its sensitivity toward friction (**1**:112 N, **1** $\cdot$ $5H_2O$: 240 N) and electrical discharge is significantly lower (**1**:0.15 J, **1**$\cdot$$5H_2O$: 1.05 J). The value of the electrical discharge sensitivity is comparable to that of the secondary explosive RDX (ca. 0.2 J) and significantly higher than that of lead azide (0.005 J). The friction and impact sensitivity

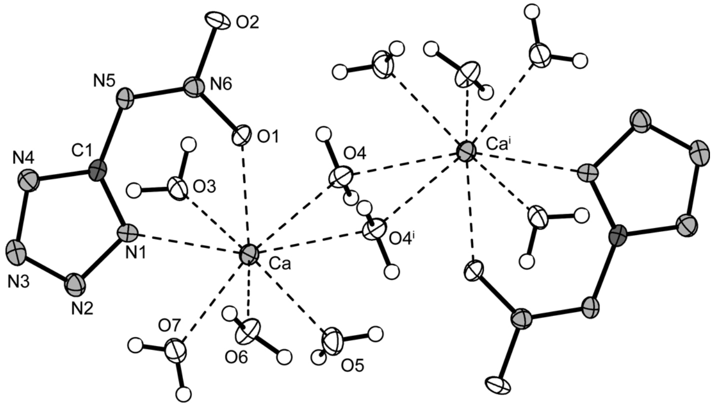


Figure 2. Molecular moiety of **1** $\cdot$ H_2O. Ellipsoids of nonhydrogen atoms are drawn at the 50% probability level. Selected coordination distances (Å): $Ca–N_1 = 2.492(2)$, $Ca–O_1 = 2.413(2)$, $Ca–O_3 = 2.516(2)$, $Ca–O_4 = 2.577(2)$, $Ca–O_5 = 2.3975(2)$, $Ca–O_6 = 2.365(2)$, $Ca–O_7 = 2.397(2)$.

values are lower than those of lead azide (Table 1), where dextrine must be used to reduce the sensitivity response. In order to assess the longevity of **1**, long-term stability tests were performed using a Systag FlexyTSC thermal safety calorimeter in combination with a RADEX V5 oven and the SysGraph Software tool (Systag, Sytem Technik AG, CH-8803, Rüschlikon, Switzerland). The tests were undertaken as long-term isoperibolic runs in glass test vessels at atmospheric pressure with 300 mg of the compound at a temperature of 265°C. Maintaining the salt for 48 hr at this temperature did not yield any decomposition reactions or mass loss.

The heat of formation $\triangle_f H^\circ$(s,M) of **1** has been calculated by the atomization energy method [5c, 21]:

$$\triangle_f H^\circ_{(g,\mathrm{M},298)} = H_{(\mathrm{Molecule},298)} - \sum H^\circ_{(\mathrm{Atoms},298)} + \sum \triangle_f H^\circ_{(\mathrm{Atoms},298)}$$

The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method described by Petersson and coworkers using the Gaussian G03 W (revision B.03) program package [21]. With the calculated gas-phase enthalpies

Table 1
Comparison of **1** with lead azide

	1	**1**·5H_2O	$Pb(N_3)_2$
Formula	$CCaN_6O_2$	$CH_{10}CaN_6O_7$	N_6Pb
Form. mass g mol^{-1}	168.13	258.23	291.23
$\rho_{\mathrm{calc.}}$/g cm^{-3}	ca. 2.0	1.9	4.8
$\triangle_f H^\circ$/kJ kg^{-1}	195.1	—	1,638
$\triangle_{\mathrm{Ex}} H^\circ$/kJ kg^{-1}	−4,632	—	−1,638
Impact sensitivity/J	5	75	2–4
Friction sensitivity/N	112	240	0.1–1 N
ESD/J	0.15	1.05	0.005
Hot plate test	Fulmination	Fulmination	Fulmination
$T_{\mathrm{dec.}}$/°C	360	360	320

(Ca^{2+}: 1,927.3 kJ mol^{-1}, $AtNO_2^{2-}$: 399.0 kJ mol^{-1}) and the lattice enthalpy ($CaAtNO_2$: 2,283.3 kJ mol^{-1}) computed by the Jenkins equation [22], $\triangle_f H^\circ$(s,M) has been calculated to be 32.8 kJ mol^{-1}. Using this value the enthalpy of explosion $\triangle_{Ex}H$ has been calculated according to the following equation and $\triangle_f H^\circ$: CaO(s) = −635.6; $\triangle_f H^\circ$, CO(g) = −110.5 kJ mol^{-1} from the literature [23] to have a great value of−778.9 kJ mol^{-1}.

$$\mathbf{1}(s) \rightarrow (CaO(s) + CO(g) + 5/2N_2(g)$$

A comparison of the energetic properties of **1** with those of commonly used lead azide is given in Table 1.

Hexanitrostilbene (HNS) is a secondary explosive with low sensitivities and a high thermal stability ($T_{dec.} = 318°C$). It can be used individually but is also manufactured as an additive to cast TNT to improve the fine crystalline structure. However, HNS is hard to initiate, and primary explosives with performances equal to or greater than silver azide are needed. Using the setup shown in Figs. 3a and 3b, we could show that **1** was

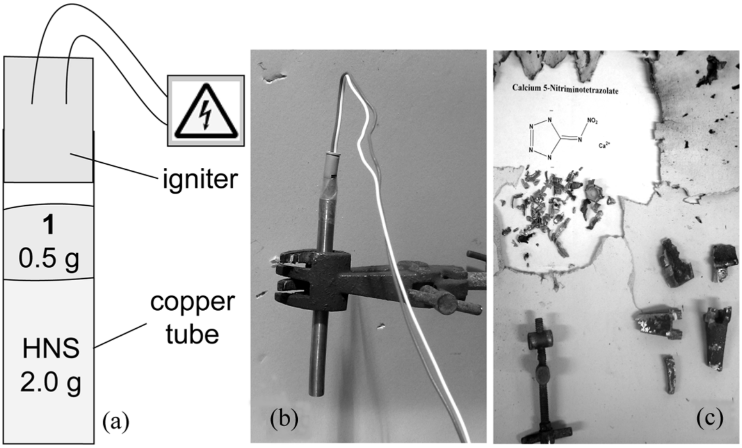


Figure 3. Initiation test of HNS using **1** as the primary explosive. (a) schematic setup; (b) experimental setup; and (c) collected fragments of initiation test.

able to initiate HNS. A standard explosive train [24] was used. A copper tube (ø = 1.0 cm) was loaded with 2 g HNS and 0.5 g **1** on the top. As igniter, an Austin Powder Firing Parameter Type I was fixed on top without direct contact to **1**. Immediately after firing the upper igniter, **1** exploded violently and an initiation of the HNS charge could be observed. The entire amount of HNS was detonated in the experiment. Larger collected fragments of the copper tube and clamp are demonstrated in Fig. 3c.

Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn: Calcium 5-nitriminotetrazolate (**1**) is a promising and powerful alternative to commonly used lead azide as a primary explosive. It shows an astonishing thermal stability up to 360°C. Its synthesis can be performed in good yields and larger scales using 5-amino-1*H*-tetrazole as starting material. Compound **1** is less polluting than lead azide because it contains no heavy metals, has a balanced oxygen content to carbon monoxide ($\Omega_{CO} = 0$) and a low solubility in water and other organic solvents. It can be detonated either by impact or electrical stimulation. The detonation wave has been proved to initiate secondary explosives such as HNS.

Acknowledgments

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[15] Synthesis starting with **2**: To 5-nitriminotetrazole (2.60 g, 20.0 mmol) dissolved in 20 mL of water, calcium hydroxide (1.48 g, 20.0 mmol) was added and the suspension was heated to 80°C and filtered off. The product was directly recrystallized from water and the crystals filtered off and washed with ethanol/ether to give 4.01 g (15.6 mmol, 78%) of calcium nitriminotetrazolate pentahydrate. DSC (5°C min^{-1},°C): 72–145°C (loss of crystal water), 360°C (explosion); IR (KBr, cm^{-1}): $\tilde{\nu} = 3{,}532$ (m), 3,360 (s), 3,309 (s), 2,167 (w), 1,647 (m), 1,622 (m), 1,559 (w), 1,540 (w), 1,474 (s), 1,412 (s), 1,338 (m), 1,299 (s), 1,158 (m), 1,135 (m), 1,087 (m), 1,042 (w), 1,026 (s), 883 (m), 835 (w), 754 (w), 722 (w), 610 (w), 566 (w); Raman (1,064 nm, 350 mW, 25°C, cm^{-1}): $\tilde{\nu} = 1{,}487$ (100), 1,431 (9), 1,406 (6), 1,220 (7), 1,160 (8),

1,138 (7), 1,091 (9), 1,047 (7), 1,029 (18), 727 (5), 611 (5), 406 (9); ^{1}H NMR (DMSO-d_6, 25°C, ppm) δ: 3.45 (s, H_2O); ^{13}C NMR (DMSO-d_6, 25°C, ppm) δ: 164.4 (CN_4); m/z (FAB$^-$): 129.1 $[HATNO_2]^-$; EA ($CaCH_{10}N_6O_7$, 258.2): calcd.: C 4.65, H 3.90, N 32.55; found: C 4.66, H 3.65, N 32.54; Sensitivities of the anhydrous compound: IS 5 J; FS $>$ 112 N; ESD $>$156 mJ.

[16] Thermogravimetry was used to investigate the dehydration step and was performed using a Setaram TG-DTA 92–16 (http://www.setaram.com/) in a helium atmosphere with a heating rate of 1°C/min to a maximum temperature of 400°C. For the measurement, 4.521 mg of pulverized **1** in a "korund" pan was used.

[17] Colorless rods, $0.15 \times 0.13 \times 0.05$, triclinic, P-1, 6.5227(2), 7.4533(1), 10.380(2) Å, 74.371(2), 72.29(2), 74.660(2)°, 453.68(16) Å^3, Z: 2, ρ_{calc}: 1.890 g cm^{-3}, μ: 0.729 mm^{-1}, F(000): 268, $\lambda_{MoK\alpha}$: 0.71073 Å, T: 200 K, τ (min–max): 3.8, 26.0°, Dataset (h; k; l): −5:8;−7:9;−9:12, Reflect. coll.: 2,373, Independ. refl.: 1,765, $R_{int} = 0.019$; Reflection obs. = 1,254, No. param.: 176, R_1 (obs): 0.0305, wR_2 (all data): 0.0665, $S =$ 0.91, Resd. Dens. [e â$^{-3}$]: −0.35, 0.45, Oxford Xcalibur3 CCD, solution: SIR-92, refinement: SHELXL-97, Absorpt. corr.: multiscan.

[18] Crystallographic data for the structure(s) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code(1223)336–033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit-@ccdc.cam.ac.uk).

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