

Research Article

Synthesis and Characterization of 5-methyl-2,4,6-trinitrobenzene-1,3-diolate and its Energetic Cesium Salt

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Abstract

The synthesis and characterization of the primary explosive cesium 5-methyl-2,4,6-trinitrobenzene-1,3-diolate (**3**) as well as its precursor compounds is described. The compounds were isolated as pure substances and characterized using multinuclear (¹H, ¹³C) NMR spectroscopy, vibrational (IR and Raman) spectroscopy, mass spectrometry and elemental analysis. The thermal behavior of the compounds was established using differential scanning calorimetry. The solid state structure of 5-methyl-2,4,6-trinitrobenzene-1,3-diol (**2**) was determined using low temperature single crystal X-ray diffraction. The friction and impact sensitivity tests were carried out using the BAM friction tester and BAM drophammer respectively. The sensitivities of the compounds towards electrostatic discharge (ESD) were determined using a small-scale ESD device (OZM). The gas phase absolute molar enthalpy at 298.15 K and 1 atm for **2** was computed applying the CBS-4M method using the GAUSSIAN 09 program package. Gas phase standard molar enthalpy of formation ($\Delta H_f^\circ(g)$) for **2** at 298 K was computed using the atomization energy method. Standard molar enthalpy of formation ($\Delta H_f^\circ(g)$) for **2** was calculated using $\Delta H_f^\circ(s)$ and the standard molar enthalpy of sublimation by applying Trouton's rule. The detonation parameters for the covalent compounds which were investigated were calculated using EXPLO5 V6.03 thermochemical computer code, using the calculated $\Delta H_f^\circ(s)$ values and the densities which were either obtained from X-ray diffraction at 298.15 K or were recalculated from values obtained at 173 K.

Keywords: Primary Explosives; Structure Elucidation; 2,4,6-Trinitro-Orcinol; Energetic Materials.

Introduction

Primary explosives are highly sensitive to different sources of stimuli (e.g. impact, friction, electrostatic discharge, light, flame, and heat). Furthermore, primary explosives show a much faster transition from deflagration to detonation (DDT) than secondary explosives and generate a detonation wave which is able to trigger high performing but less sensitive secondary explosives or propellants [1]. The first primary explosive that found widespread application was mercury fulminate (MF), which was used by Alfred Nobel in metal blasting cap detonators to initiate dynamite [1-9]. During the last century, MF was replaced by lead azide (LA) and lead styphnate (LS) which show lower toxicity, improved performance and better thermal stability [10-14]. LA has many advantageous

properties which make it still the most commonly used primary explosive: LA is resistant to heat and moisture, not very hygroscopic, more effective than MF even in smaller quantities, higher triggering rate than MF. Moreover, in contrast to MF, LA cannot be dead pressed [11, 13, 15].

Unfortunately, LA is highly sensitive to friction and needs to be phlegmatized [1, 13]. Moreover, it slowly decomposes in presence of moist air containing carbon dioxide to form an extremely toxic hydrazoic acid (HN₃) and basic lead carbonate [13,16]. Hydrazoic acid can further react with the copper metal in the encapsulating casing to give the highly sensitive to impact and friction copper(II) azide [13,16]. LA decomposes in the presence of acids [13,17]. Finally, the environmental concerns associated with the toxicity of lead are also one of the

most important drawbacks of LA [13,16].

Therefore, research concerned with finding suitable replacements for lead-containing primary explosives is an essential aspect of present investigations in the energetic materials field. For a compound to be considered as a possible LA replacement, it has to meet the following minimum requirements: (a) insensitivity to light; (b) sensitivity to detonation but not too sensitive to handle and transport; (c) thermal stability of at least 200 °C, (d) chemically stable for long periods time; (e) free of toxic metals; and (f) free of toxic perchlorate [18].

Among recently synthesized metal-containing ionic primary explosives, the following are the promising candidates for possible application as primary explosives: iron and copper complexes of the type $[\text{cat}]^+_2[\text{M}(\text{NT})_4(\text{H}_2\text{O})_2]$ ($[\text{cat}]^+ = \text{NH}_4^+, \text{Na}^+$; $\text{M} = \text{Fe}^{2+}, \text{Cu}^{2+}$; $\text{NT} = 5\text{-nitrotetrazolate}$) [18], copper(II) bis(1-methyl-5-nitriminotetrazolate) [19], copper(I) 5-nitrotetrazolate (DBX-1) [20], calcium 5-nitriminotetrazolate [21], potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate-3-oxide (KDNP) [22] and potassium 1,1'-dinitramino-5,5'-bis(tetrazolate) ($\text{K}_2\text{D-NABT}$) [23].

Until now mostly investigated energetic materials containing in the chemical structure both 2,4,6-trinitrobenzene and hydroxy functionalities were based on picric acid (PA) and styphnic acid (SA) (Figure 1).

Building on our current extensive research in the field of energetic materials, we decided to focus on decreasing sensitivity to external stimuli of 2,4,6-trinitrobenzene-1,3-diol (SA) based salts, by inserting a methyl group in the five-position of the benzene ring (5-methyl-2,4,6-trinitrobenzene-1,3-diol, TNO - Figure 1).

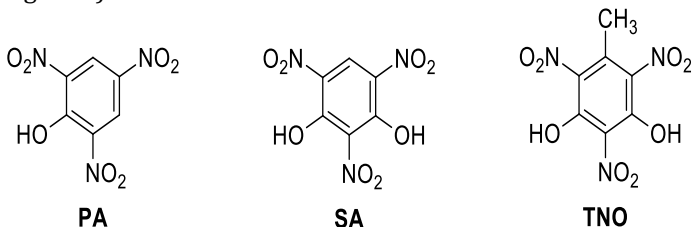


Figure 1. Chemical structures of PA, SA and TNO.

Synthesis of PA from phenol using nitric acid was reported in 1841 by Laurent [24]. In 1871 Sprengel reported that PA can be detonated [25]. The explosive power of picric acid is slightly superior to that of 2,4,6-trinitrotoluene (TNT) [15]. The main drawback of PA is its tendency to form impact sensitive metal salts (picrates) when it is in direct contact with metal shell walls [15]. Among investigated picric acid salts, the most known are lead picrate which was used in various initiating compositions and in mixtures for electric fuse heads [14]. Handling of anhydrous lead picrate has the same risk level as the handling of LS [14]. Unfortunately, the environmental concerns associated with the toxicity of lead excluded the further practical application of lead picrate. SA is a relatively weak ex-

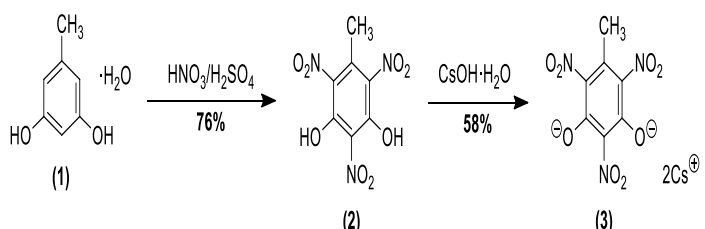
plosive which can be obtained *via* nitration of either resorcinol or 2-nitroresorcinol using sulfuric acid and potassium nitrate [15,26]. The most important salt of SA is described above LS. Barium styphnate is not very sensitive to impact and its brisance is lower than for LS [14]. It is used in delay compositions, as an ingredient of primary compositions [14]. The silver styphnate is characterized by sensitivity to impact similar to LS and high sensitivity to flame. It has been proposed as a primary explosive [14].

Herein, we present the synthesis and investigation of 5-methyl-2,4,6-trinitrobenzene-1,3-diolate and its energetic cesium salt. The nitration of 3,5-dihydroxytoluene monohydrate using a mixture of concentrated nitric acid and concentrated sulphuric acid was performed accordingly to the methodology presented by Marchand and Reddy [27] while synthesis and characterization of the cesium salt are presented for the first time.

Results and Discussion

Synthesis

The first step in the synthesis of cesium 5-methyl-2,4,6-trinitrobenzene-1,3-diolate (**3**) is the nitration of 3,5-dihydroxytoluene monohydrate (**1**) using concentrated nitric and sulfuric acids to form 5-methyl-2,4,6-trinitrobenzene-1,3-diol (**2**) following a modified method of Marchand and Reddy [27]. The next step is the reaction of **2** with cesium hydroxide monohydrate to give the final product **3** (Scheme 1).



Scheme 1. Synthesis of cesium 5-methyl-2,4,6-trinitrobenzene-1,3-diolate (**3**).

Single-crystal X-ray analysis

The single crystal X-ray diffraction dataset of **2** was collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA), enhanced molybdenum K_α radiation source ($\lambda = 0.71073 \text{ \AA}$), Oxford Cryostream cooling unit, four circle kappa platform and a Sapphire CCD detector. By using the CRYALISPRO software, the data collection and reduction were performed [28]. The structure was solved with SIR-97 [29], refined by full-matrix least-squares on F^2 with SHELXL 97 [30,31], and checked with PLATON [32-34], which are all integrated within the WINGX software suite [35]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The finalized CIF file was checked with checkCIF [36]. Illustrations of mo-

lecular structures were drawn with DIAMOND 4 [37]. CCDC 1476881 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

5-Methyl-2,4,6-trinitrobenzene-1,3-diol (**2**) crystallizes from ethyl acetate in the orthorhombic space group $P2_12_12_1$ with a calculated density of 1.759 g cm^{-3} at 123 K and four molecules in the unit cell (Table 1). The molecular structure of **2** is shown in Figure 2.

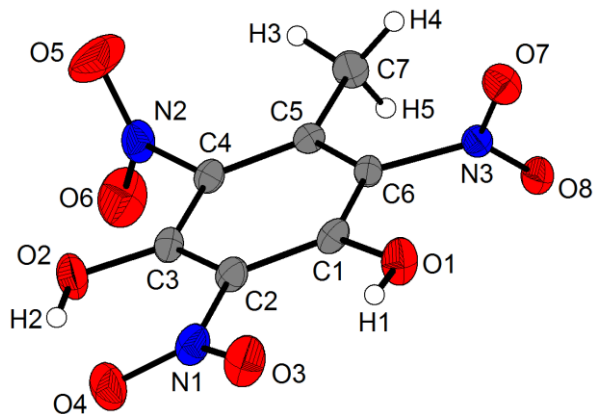


Figure 2. Molecular structure of 5-methyl-2,4,6-trinitrobenzene-1,3-diol (**2**) in the crystal. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii. Selected bond lengths [Å]: C1–C2 1.414(3), C1–C6 1.389(2), C1–O1 1.332(2), C2–C3 1.403(3), C2–N1 1.443(3), C3–C4 1.390(3), C3–O2 1.335(3), C4–C5 1.390(3), C4–N2 1.464(2), C5–C6 1.387(2), C5–C7 1.501(3), C6–N3 1.468(2), N1–O3 1.232(2), N1–O4 1.236(3), N2–O5 1.214(3), N2–O6 1.210(3), N3–O7 1.227(2), N3–O8 1.220(2). Selected bond angles [°]: C1–C6–N3 115.4(2), C2–C1–O1 124.9(2), C2–N1–O3 119.0(2), C2–N1–O4 118.7(2), C3–C2–N1 120.1(2), C4–C3–O2 116.0(2), C4–N2–O5 117.1(2), C4–N2–O6 118.5(2), C5–C4–N2 119.7(2), C6–C5–C7 122.8(2), C6–N3–O7 117.5(2), C6–N3–O8 118.1(2).

	2
Chemical formula	$\text{C}_7\text{H}_5\text{N}_3\text{O}_8$
Molecular weight [$\text{g}\cdot\text{mol}^{-1}$]	259.14
Color, habit	pale yellow rod
Size [mm]	0.40x0.10x0.03
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a [Å]	5.5309(2)
b [Å]	8.0469(3)
c [Å]	21.9802(8)
α [°]	90
β [°]	90
γ [°]	90
V [Å ³]	978.26(6)
Z	4
ρ_{calc} [$\text{g}\cdot\text{cm}^{-3}$]	1.759
μ [mm^{-1}]	0.165
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073
$F(000)$	528
θ min-max [°]	4.125–30.499
T [K]	123(2)
Dataset h	$-7 \leq h \leq 7$
Dataset k	$-11 \leq k \leq 11$
Dataset l	$-31 \leq l \leq 31$
Reflections collected	10066
Independent reflections	2973
Observed reflections	2627
Number of parameters	173
R_{int}	0.0303
GoF on F^2	1.062
R_1, wR_2 ($I > \sigma I_0$)	0.0366, 0.0866
R_1, wR_2 (all data)	0.0446, 0.0925

Weighting scheme (x, y) ^[a]	0.0419, 0.1917
Remaining density [e·Å ⁻³]	-0.191, 0.267
Device type	Oxford XCalibur3 CCD
Solution	SIR-97
Refinement	SHELXL-97
Absorption correction	multi-scan
CCDC	1476881

$${}^{[a]}wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]\} \text{ where } w = 1 / [\sigma_c^2(F_o^2) + (xP)^2 + yP] \text{ and } P = (F_o^2 + 2F_c^2) / 3$$

Table 1. Crystallographic data and refinement parameters of **2**.

In the solid state structure of **2**, the *ortho*-nitro groups are significantly twisted out of the benzene ring plane ($\angle C5-C4-N2-O6$, 101.8(2)°; $\angle C5-C6-N3-O7$ 114.1(2)°), while the *para*-nitro group is only slightly twisted out of the ring plane ($\angle C1-C2-N1-O3$, 7.9(3)°). Two strong intramolecular O-H...O hydrogen bonding interactions are observed in the solid state structure of **2** (Table 2), which are similar to those reported for the related compound 5-methoxy-2,4,6-trinitro-1,3-benzenediol by Deschamps and Straessler [38].

D-H...A	d(D-H) [Å]	d(H...A) [Å]	d(D...A) [Å]	$\angle DHA$ [°]
O1-H1...O3	0.78(4)	1.93(4)	2.570(2)	139(4)
O2-H2...O4	0.83(3)	1.88(3)	2.591(2)	143(3)

Table 2. Intramolecular hydrogen bonds within the crystal structure of **2**.

Thermal Stabilities and Sensitivities

The thermal stabilities of **2**, and **3** were measured using differential scanning calorimetry (DSC, $\beta = 5$ °C·min⁻¹). Thermal decomposition of **2** occurs at 223 °C (onset value) while compound **3** exhibits superior thermal stability with an onset value for exothermic decomposition at 255 °C.

For initial safety testing, the impact, friction, and electrostatic discharge sensitivities were determined. The impact sensitivity of **2** was measured to be 17.5 J and the friction sensitivity is lower ($FS > 360$ N) than the measuring range of the friction tester apparatus. In terms of *IS* and *FS*, **2** is less sensitive than picric acid (PA) and styphnic acid (SA). Moreover, **2** shows low sensitivity to electrostatic discharge ($ESD = 0.75$ J; typical values for the human body are within the range 5 – 20 mJ) [1]. The lower sensitivities of **2** to external stimuli make it a suitable starting material for the synthesis of primary explosives.

The cesium salt (**3**) is much more sensitive to impact ($1 < IS < 2$ J; $IS_{LA} = 2.4$ J[1]), friction ($FS = 24$ N; $FS_{LA} = 0.1$ N[1]), and electrostatic discharge ($ESD = 5$ mJ; $ESD_{LA} = 4.7$ mJ[1]) than its precursor **2**. Based on this data, **3** can be placed in the most sensitive classes in terms of its both friction and impact sensitivity according to the UN Recommendations on the Transport of Dangerous Goods (*impact: insensitive >40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; friction: insensitive >360 N, less sensitive = 360 N, sensitive <360 N and >80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N*) [39].

A preliminary flame test using a small amount of **3** (approximately 5 mg) - in which the compound was heated on a spatula using a lighter but without direct flame contact - showed that compound **3** detonated upon reaching its ignition temperature.

Energetic Properties

The gas-phase absolute molar enthalpy at 298 K and 1 atm for **2** were calculated theoretically using the modified complete basis set method (CBS-4M) with the GAUSSIAN 09 software [40-42]. The atomization-energy method was applied in order to calculate the gas phase standard molar enthalpy of formation ($\Delta H_f^\circ(g)$) at 298.15 K [42-45]. In order to obtain the standard molar enthalpy of formation ($\Delta H_f^\circ(s)$) the value of the standard molar enthalpy of sublimation (estimated using Trouton's rule) was subtracted from $\Delta H_f^\circ(g)$ [46, 47]. The values of $\Delta H_f^\circ(s)$ for PA and SA were taken from the literature (Table 3) [48, 49].

The Chapman-Jouguet (C-J) characteristics (detonation temperature, detonation pressure, detonation velocity) for the precursor (**2**) of the primary explosive (**3**), were calculated using EXPLO5 V6.03 thermochemical computer code [50]. Additionally, for comparison reasons, calculations were also performed for PA and SA (Table 4).

The detonation parameters were calculated based on the $\Delta H_f^\circ(s)$ values and the densities using the EXPLO5 V6.03 thermochemical computer code [50]. In the cases of PA and SA, the theoretical maximum densities obtained from X-ray diffraction measurements at 298 K were used [51, 52], while for **2**, the density was re-calculated from the single crystal density determined at 123 K using the Equation 1 [53] and the coefficient of volume expansion (α_v) of 2,4,6-trinitrotoluene (the orthorhombic form, $\alpha_v = 19.8 \times 10^{-5}$ K⁻¹) [54].

$$\rho_{298} = \frac{\rho_T}{1 + \alpha_v(298 - T)} \quad (1)$$

The calculations for explosives assume ideal behavior and estimation of the detonation parameters is based on the chemical equilibrium steady-state model of detonation [50]. The thermodynamic functions of the detonation products in the standard state are calculated from the enthalpy (which is expressed in a fourth-degree polynomial form as a function of temperature) [50]. The Becker-Kistiakowsky-Wilson equation

of state (BKW EOS) with the BKWN set of constants: $\alpha = 0.5$, $\beta = 0.38$, $\kappa = 9.4$, and $\theta = 4120$ for gaseous detonation products, and the Murnaghan equation of state for condensed products (compressible solids and liquids) were applied [50]. The calculation of the equilibrium composition of the detonation products uses a modified version of White, Johnson and Dantzig's free energy minimization technique [50].

	PA	SA	2
Formula	$C_6H_3N_3O_7$	$C_6H_3N_3O_8$	$C_7H_5N_3O_8$
$IS^{[a]}$ [J]	7.4[15]	7.4[15]	17.5
$FS^{[b]}$ [N]	> 353[15]	353[15]	> 360
$ESD^{[c]}$ [J]	nd	nd	0.75
$N^{[d]}$ [%]	18.34	17.15	16.22
$O^{[e]}$ [%]	-45.39	-35.9	-52.48
$T_m^{[f]}$ [°C]	122 (I polymorph)[55] 105 (II polymorph)[55] 75 (III polymorph)[55]	181.6[56]	172
$T_{dec}^{[g]}$ [°C]	nd	nd	223
$\rho^{[h]}$ [g·cm ⁻³]	1.769[51]	1.829[52]	1.700
$\Delta H_f^{[i]}$ [kJ·mol ⁻¹]	-218[48]	-468[49]	-410

[a] Impact sensitivity (BAM drophammer, method 1 of 6); [b] friction sensitivity (BAM drophammer, method 1 of 6); [c] electrostatic discharge device (OZM research); [d] nitrogen content; [e] oxygen balance; [f] Melting point; [g] temperature of decomposition; [h] density at 298 K; [i] standard molar enthalpy of formation.

Table 3. Physico-chemical properties of PA, SA and 2.

EXPLO5 V6.03	PA	SA	2
$- \Delta_E U^{[j]}$ [kJ·kg ⁻¹]	4537	4146	4079
$T_{C-J}^{[k]}$ [K]	3440	3203	3091
$P_{C-J}^{[l]}$ [GPa]	23.4	24.0	20.1
$V_{C-J}^{[m]}$ [m·s ⁻¹]	7436	7522	6986
Gas vol. ^[n] [dm ³ ·kg ⁻¹]	631	623	641

[j] heat of detonation; [k] detonation temperature; [l] detonation pressure; [m] detonation velocity; [n] volume of detonation gases at standard temperature and pressure conditions.

Table 4. The C-J characteristics of PA, SA and 2 calculated using EXPLO5 V6.03.

Conclusions

The introduction of the second hydroxy group to the PA molecule has practically no influence on the IS and FS. However, SA has a higher melting point, density, and oxygen balance than PA. Incorporation of the methyl group in the five-position of the SA molecule results in a decrease in the sensitivities to external stimuli (IS, FS). This is of great importance in terms of safety. The presence of the methyl group in 2 results in a reduction in the nitrogen content, oxygen balance, and density compared to PA and SA. The lower density and the relatively low enthalpy of formation of 2 are reflected in the lower values of the detonation parameters of 2. Nevertheless, these important factors are still relatively high, and therefore 2 could be used as a starting material in the synthesis of energetic salts.

The cesium salt (3) is characterized by high decomposition temperature (255 °C, onset). Sensitivity investigations show that 3 is more sensitive to impact than LA, electrostatic sensitivity is in the range of LA while its sensitivity to friction is much lower than this determined for LA. The preliminary flame test and sensitivity to external stimuli measurements show that 3 have properties of a primary explosive. Further research in order to determine the ability to initiate of detonation in secondary explosives has to be performed.

Experimental Part

General Procedures: All reagents and solvents were used as received (Sigma Aldrich, Fluka, Acros Organics), if not stated otherwise. Differential Scanning Calorimetry (DSC) was performed on a LINSEIS DSC PT10 with about 1 mg substance in a perforated aluminum vessel with a heating rate of 5 K·min⁻¹ and a nitrogen flow of 5 dm³·h⁻¹. ¹H NMR and ¹³C NMR spectra were recorded with a JEOL Eclipse 400 ECX instrument. Chemical shifts are given in parts per million relative to tetramethylsilane. The solvent residue signal was used as a locking signal for ¹H NMR and ¹³C{¹H} NMR spectroscopy. Infrared spectra were measured with a Perkin-Elmer Spectrum BX FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. Raman spectra were recorded using a Bruker MultiRAM FT-Raman instrument fitted with a liquid-nitrogen-cooled germanium detector and a Nd:YAG laser ($\lambda = 1064$ nm). Low-resolution mass spectra were recorded with a JEOL MStation JMS 700 (DEI+ / FAB+/-). Elemental analysis was carried out using a Vario Micro from the Elementary Company. Sensitivity data were determined using a BAM (Bundesanstalt für Materialforschung) drop hammer and a BAM friction tester. The electrostatic sensitivity tests were performed using an Electric Spark Tester ESD 2010 EN from OZM Research.

CAUTION! All materials prepared are energetic compounds with sensitivities to various stimuli and only small quantities should be prepared and handled. Although we encountered no issues in the handling of these materials, proper protective measures (e.g., face shield, ear protection, body armor, Kevlar gloves,

and earthed equipment) should be used, especially if working with primary explosive 3.

5-Methyl-2,4,6-trinitrobenzene-1,3-diol (2)[27]

A mixture of concentrated sulfuric (14.0 mL) and concentrated nitric (2.8 mL) acids was cooled to 0 °C. Subsequently, 3,5-dihydroxytoluene monohydrate (4.0 mmol, 568 mg) was dissolved in concentrated sulfuric acid (10 mL) and added slowly in a dropwise manner to the cooled acids. After addition was complete, the reaction mixture was stirred for 1 h at 0 °C. Afterward, the mixture was poured onto crushed ice (50 mL). The product was extracted from the aqueous phase with ethyl acetate (4 x 50 mL). The extract was evaporated under low pressure. Finally, after drying under high vacuum, the desired product was obtained as fine yellow rods (yield 790 mg, 76%). **DSC** (5 °C·min⁻¹): 172 °C (melt., onset), 223 °C (dec., onset); **¹H NMR** (400.13 MHz, [D₆]DMSO, 26 °C) δ: 10.66 (s, 2H, OH), 2.25 (s, 3H, CH₃), ppm; **¹³C{¹H} NMR** (100.6 MHz, [D₆]DMSO, 26 °C) δ: 152.5, 131.9, 131.4, 129.3, 15.9, ppm; **IR** (ATR, 25 °C, cm⁻¹) $\tilde{\nu}$: 3228 (w), 1608 (m), 1590 (s), 1535 (vs), 1461 (w), 1419 (m), 1362 (vs), 1306 (s), 1258 (m), 1160 (vs), 1144 (vs), 1067 (m), 1045 (m), 914 (w), 897 (s), 829 (w), 802 (m), 784 (s), 751 (m), 739 (m), 717 (w), 694 (s); **Raman** (1064 nm, 300 mW, 25 °C, cm⁻¹) $\tilde{\nu}$: 2938 (4), 1633 (18), 1540 (10), 1364 (27), 1305 (100), 1273 (11), 1184 (12), 829 (44); **MS (DEI⁺)**: *m/z* = 259.0 [M]⁺; **elemental analysis** calcd (%) for C₇H₅N₃O₈, 259.13: C 32.45, H 1.94, N 16.22; found C 32.44, H 1.97, N 16.19; **BAM drophammer**: 17.5 J (<100 μm); **friction tester**: >360 N (<100 μm); **ESD**: 0.75 J (<100 μm).

Cesium 5-methyl-2,4,6-trinitrobenzene-1,3-diolate (3)

5-Methyl-2,4,6-trinitrobenzene-1,3-diol (0.48 mmol, 124 mg) was dissolved in 20 mL of ethanol and a solution of cesium hydroxide monohydrate (0.96 mmol, 161 mg) in 5 mL of ethanol was added dropwise. During the addition of the cesium hydroxide solution, a red solid immediately precipitated. After addition of the hydroxide was complete, the reaction mixture was heated for 2 hours under reflux. The precipitate was then filtered off and dried under high vacuum yielding red platelets (yield 145 mg, 58%). **DSC** (5 °C min⁻¹): 255 °C (dec., onset); **¹H NMR** (400.13 MHz, [D₆]DMSO, 26 °C) δ: 1.97 (s, 3H, CH₃), ppm; **¹³C{¹H} NMR** (100.6 MHz, [D₆]DMSO, 26 °C) δ: 161.3, 135.6, 131.2, 128.5, 16.1, ppm; **IR** (ATR, 25 °C, cm⁻¹) $\tilde{\nu}$: 2996 (vw), 1567 (vs), 1513 (w), 1494 (m), 1467 (m), 1412 (m), 1384 (w), 1376 (w), 1287 (s), 1232 (vs), 1180 (vs), 1047 (s), 1026 (m), 922 (m), 811 (w), 786 (s), 756 (m), 738 (w), 724 (s), 692 (s), 675 (s); **Raman** (1064 nm, 300 mW, 25 °C, cm⁻¹) $\tilde{\nu}$: 3006 (2), 2948 (3), 1423 (7), 1379 (7), 1295 (100), 1053 (10), 815 (91), 697 (7); **MS (FAB⁺)**: *m/z* = 133.1 [Cs]⁺; **MS (FAB⁻)**: *m/z* = 258.2 [C₇H₄N₃O₈]⁻; **elemental analysis** calcd (%) for C₇H₃N₃O₈Cs₂, 522.92: C 16.08, H 0.58, N 8.04; found: C 16.03, H 0.58, N 7.98; **BAM drophammer**: 1 2 J (<100 μm); **friction tester**: 24 N (<100 μm); **ESD**: 5 mJ (<100 μm).

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